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THE THERMODYNAMICS OF THE RHENIUM-OXYGEN AND MOLYBDENUM-OXYGEN SYSTEMS AND THE DEFECT STRUCTURE OF ALPHA TANTALUM PENTOXIDE

DISSERTATION

Presented in Partial Fulfillment of the requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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******

The Ohio State University
1964

Approved by

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Dedicated to my devoted wife, Jane Ann, for her encouragement and sacrifice in helping to complete this work, and to my son, Chris, for the tears he so often shed when I left and the smiles he always gave when I returned.
ACKNOWLEDGMENTS

Many people, professors, administrators, and fellow students have made contributions to my education, and, thus, either directly or indirectly to this work. A sincere thanks goes to all of these people. Only a few, those who made major contributions to this work, are acknowledged here.

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INTRODUCTION

The oxidation of metals is an area of considerable activity in metallurgical engineering. The rate of reaction between a metal and the oxidizing gases in the environment of its application often determines whether or not the metal is a useful engineering material. The refractory metals, tungsten, tantalum, niobium, molybdenum, and rhenium, have very high melting points and good strength properties at temperatures well above the upper temperature limits for the iron, nickel, and cobalt base alloys. These metals would be useful at very high temperatures except for their uniformly poor resistance to attack by oxidizing gases. Their behavior varies from the formation of volatile oxides to autogeneous combustion. Faced with this problem, the engineer may attempt to determine the oxidation mechanism and then try to alter the rate-controlling steps in the reaction. This is a fundamental approach to the oxidation problem.

To determine the oxidation mechanism for a metal one needs to know, among other things, the stability ranges of the oxides formed and the transport characteristics of each
oxide. The stability ranges of the oxides are determined by the thermodynamics of the metal-oxygen system. The transport characteristics of an oxide are often dependent on its defect structure. The defect structure is the composite of point defects present in the oxide. These point defects may be vacant oxygen or metal sites, interstitial oxygen or metal atoms, etc., and any of these defects may be ionized, contributing electrons to the electrical conduction processes of the oxide. The defects directly participate in the diffusion processes and may be considered to be the mobile species. Usually only one type of defect is present in a particular oxide for a given temperature and oxygen potential. The defect structure of an oxide may be determined by studying the electrical resistance or thermoelectric power over a range of oxygen potentials and temperatures. This method works when the defects are partially or completely ionized and the intrinsic conductivity of the oxide is relatively small. An alternative method that will work in most cases is the gravimetric technique in which the weight of an oxide sample is monitored over a range of oxygen potentials and temperatures. The identity of the defect is determined from the exponential relationship between the resistance, thermoelectric power, or weight and the oxygen potential at constant temperature. The relationship between the resistance, thermoelectric power, or weight and temperature at constant oxygen
potential determines the activation energy for the formation of the defects.

In any defect structure investigation, it is essential that the experimental conditions of oxygen potential and temperature be varied only within the range where the oxide being studied is stable. The stability range for an oxide is fixed by the thermodynamic equilibria between the oxide and the phases both higher and lower in oxygen content. Thus, one must have a knowledge of the thermodynamics of the metal-oxygen system before attempting to determine the transport characteristics of any of the oxides. Otherwise, one could not be certain that the oxide being studied was actually present in the experimental environment. One should also be aware that side reactions may make it difficult or even impossible to determine the defect structure of certain oxides. For example, when using CO-CO$_2$ gas mixtures to fix the oxygen potential, the possibility of carbide formation arises. Therefore, before undertaking a defect structure determination, the investigator should have a thorough knowledge of the thermodynamics of the metal-oxygen system; and he should be cautious in designing his experiments to prevent his measurements from being rendered useless by some extraneous reaction.

This work was undertaken because of strong interests in both the thermodynamics of metal-oxygen systems and the defect structures of oxides. The refractory metals area
was chosen primarily because it is an area where much work is needed. Knowledge of the thermodynamics of the rhenium-oxygen and molybdenum-oxygen systems has been extended by this work, and the defect structure of alpha-tantalum pentoxide has been elucidated. Perhaps these contributions will help in resolving the oxidation mechanism of the refractory metals, ultimately leading to the extended use of these metals at high temperatures.
THERMODYNAMICS OF THE RHENIUM-OXYGEN SYSTEM

Introduction

Rhenium has a melting point of 3180°C which is second only to tungsten among all metals. Even though its melting point is higher than those of tantalum, niobium, and molybdenum, rhenium is not normally classified as a refractory metal. The reasons for this are not clear although rhenium has a different crystal structure and costs more than the four common refractory metals, tungsten, tantalum, niobium, and molybdenum.

Rhenium oxidizes rapidly in air or oxygen forming volatile Re$_2$O$_7$ even at relatively low temperatures. However, the oxidation behavior of rhenium is not much worse than that of the main four refractory metals, and, in fact, it is similar to the behavior of molybdenum and tungsten in many respects.

The occurrence of rhenium in the earth's crust is very rare. Rhenium appears mainly with molybdenum in concentrations of the order of one gram per ton. The resulting very high production costs cause most metallurgists to place rhenium in the precious metals group along with platinum, gold, and so forth. It would seem that if production
costs are reduced at some time in the future, rhenium will then be grouped with the refractory metals. Perhaps it would be a good compromise to call rhenium a refractory-precious metal.

Few oxidation studies on rhenium have been carried out, and only a fraction of the thermodynamic data needed to calculate the equilibria in the rhenium-oxygen system have been determined. The initial purpose of this investigation was to determine whether oxygen potentials in the stability ranges of any of the rhenium oxides could be fixed by using such gas mixtures as hydrogen and water vapor. After some preliminary tests it became obvious that the gas mixtures required could not be achieved through conventional techniques, and, thus, it would not be possible to determine the defect structures of rhenium oxides. However, the main phase of the investigation, the determination of the free energy of formation of rhenium dioxide, was carried to completion. Several qualitative experiments were done to check some information in the current literature. Part of this information was found to be either inaccurate or completely wrong.

There is a lack of data in some areas, but it is possible to fix some of the thermodynamic functions using the several good investigations reported in the literature and this work. These functions have been used as the basis for a tentative set of thermodynamic functions for the
entire rhenium-oxygen system. The areas where additional work is needed have been pointed out, and, when some additional work is completed, it is likely that a consistent thermodynamic description of the rhenium-oxygen system will be possible.

Literature Survey

The physical, mechanical, and chemical properties of rhenium have been recently reviewed in the books by Gonser,¹ and by Lebedev.² The book edited by Gonser,¹ Rhenium, contains much general information on the metallurgy and chemistry of rhenium, while The Chemistry of Rhenium by Lebedev² is devoted principally to geochemistry, extraction, and preparation. Some properties of rhenium are listed in Table 1.

Table 1
Properties of Rhenium

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>75</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>186.31</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>h.c.p.</td>
</tr>
<tr>
<td>Lattice constants (20°C)</td>
<td>(a = 2.760 \pm 0.001 \text{ Å})\n</td>
</tr>
<tr>
<td>Melting point</td>
<td>3180°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>5900°C</td>
</tr>
<tr>
<td>Density</td>
<td>21.04 g/cc</td>
</tr>
<tr>
<td>Specific heat (25°C)</td>
<td>6.143 cal/g-atom/°K</td>
</tr>
</tbody>
</table>
Solubility of oxygen in rhenium

The maximum solubility of interstitial oxygen in rhenium has been estimated to be 12 ppm, based on an analysis of the behavior of transition metals. 3

Rhenium oxides

Seven oxides of rhenium have been proposed: Re$_2$O$_5$, ReO, Re$_2$O$_3$, ReO$_2$, ReO$_3$, Re$_2$O$_7$, and Re$_2$O$_8$. Young and Irvine$^4$ prepared hydrates of Re$_2$O$_5$ and ReO, but neither was obtained in pure state. Druce$^5$ states that Re$_2$O$_5$, ReO, and Re$_2$O$_3$ are all hydrates and that the existence of Re$_2$O$_8$ is doubtful. Ogawa$^6$ claimed to measure the vapor pressure of Re$_2$O$_8$, but his work has been disputed by Woolf$^7$ who believes that a fine spray of perrhenic acid caused by the presence of moisture may have been mistaken for Re$_2$O$_8$. The existences of ReO$_2$, ReO$_3$, and Re$_2$O$_7$ have all been well established. Tribalat, Jungfleisch, and Collet$^8$ prepared Re$_2$O$_7$ by heating Re in oxygen, ReO$_3$ by heating pure Re$_2$O$_7$ to 150°C in dioxane, and ReO$_2$ by heating ReO$_3$ to 650°C–680°C in a vacuum. In their investigation only ReO$_2$, ReO$_3$, and Re$_2$O$_7$ were found. No oxides other than ReO$_2$, ReO$_3$, and Re$_2$O$_7$ were obtained by Deschanvres$^9$ who used radiocrystallographic and chemical analysis to study oxygenated rhenium compounds.

Magneli$^{10}$ confirmed the existence of ReO$_2$ and ReO$_3$. ReO$_2$ was obtained by heating Re and ReO$_3$ or Re$_2$O$_7$ together
in a closed capsule at 800°C for two days. The methods of preparation of ReO$_3$ and Re$_2$O$_7$ are extensively described by Audrieth.\textsuperscript{11}

The crystal structures of ReO$_2$, ReO$_3$, and Re$_2$O$_7$ have been determined and are listed in Table 2.

Table 2
Crystal Structures of Rhenium Oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Crystal Symmetry</th>
<th>Unit Cell Dimensions</th>
<th>Space Group</th>
<th>Cell Content</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO$_2$</td>
<td>orthorhombic</td>
<td>$a = 4.810 \text{ Å}$</td>
<td>Pbcn</td>
<td>4ReO$_2$</td>
<td>Magneli$^{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b = 5.643 \text{ Å}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 4.601 \text{ Å}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ReO$_3$</td>
<td>cubic</td>
<td>$a = 3.734 \text{ Å}$</td>
<td>Pm3m</td>
<td>ReO$_3$</td>
<td>Meisel$^{13}$</td>
</tr>
<tr>
<td>Re$_2$O$_7$</td>
<td>orthorhombic</td>
<td>$a = 15.25 \text{ Å}$</td>
<td>Pmnc</td>
<td>8Re$_2$O$_7$</td>
<td>Wilhelmi$^{14}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b = 5.48 \text{ Å}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 12.5 \text{ Å}$</td>
<td></td>
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</tr>
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</table>

A monoclinic form of ReO$_2$ has been reported by Magneli.\textsuperscript{10} This is not stable above 300°C as it converts into the orthorhombic phase. Magneli and Marinder$^{15}$ have studied both forms of ReO$_2$, and they found short metal-metal distances which indicate the presence of intermetallic bonds. The short metal-metal distances are within zigzag strings of ReO$_6$ octahedra joined at the edges, and the strings are connected by octahedra sharing corners.\textsuperscript{10} Meisel$^{13}$ determined that ReO$_3$ is a cubic arrangement of ReO$_6$ octahedra joined by sharing corners.
Thermodynamic investigations of rhenium and rhenium oxides

Smith, Oliver, and Cobble\textsuperscript{16} determined the low temperature heat capacity of rhenium and found $C_{\text{p},298.16} = 6.143 \text{ cal/g-atom/}^\circ\text{K}$ and $S_{298.16}^0 = 8.89 \pm 0.03$ e.u. K. K. Kelly\textsuperscript{17} gives the following equation for the heat capacity of rhenium, $C_p = 5.66 + 1.3(10)^{-3}T$ cal/g-atom/\(^\circ\text{K}$). This equation gives slightly lower values than those found by Smith, Oliver, and Cobble\textsuperscript{16} with a difference of 0.095 cal/g-atom/\(^\circ\text{K}$ at 298.16\(^\circ\text{K}$). The heat capacity of crystalline Re\textsubscript{2}O\textsubscript{7} was studied by Busey\textsuperscript{18} who found $C_{\text{p},298.16} = 39.73 \text{ cal/g-atom/}^\circ\text{K}$ and $S_{298.16}^0 = 49.54 \pm 0.05$ e.u. No other heat capacity data were found for the rhenium oxides.

Roth and Becker\textsuperscript{19} were the first to determine the standard heats of formation of rhenium oxides, and they reported $\Delta H_f^0 = -297.5 \pm 2 \text{ Kcal/mole}$ for Re\textsubscript{2}O\textsubscript{7} and $\Delta H_f^0 = -82.5 \pm 10\% \text{ Kcal/mole}$ for ReO\textsubscript{3}. The latter value was certainly much in error as Boyd, Cobble, and Smith\textsuperscript{20} found $\Delta H_f^0 = -146.0 \pm 3.0 \text{ Kcal/mole}$ for ReO\textsubscript{3} by combustion of Re and ReO\textsubscript{2}. Roth and Becker\textsuperscript{19} estimated the heat of formation of ReO\textsubscript{3} from the amounts of ReO\textsubscript{3} found in samples of Re\textsubscript{2}O\textsubscript{7} that did not undergo complete combustion. Boyd, Cobble, and Smith\textsuperscript{20} found $\Delta H_f^0 = -295.9 \pm 2.0 \text{ Kcal/mole}$ for Re\textsubscript{2}O\textsubscript{7} which is in good agreement with the work of Roth and Becker.\textsuperscript{19} King and Cobble\textsuperscript{21} later determined the standard heat of formation of ReO\textsubscript{3} with measurements of the potential
of the ReO$_2$/ReO$_4^-$ electrode. The value they found was 
$\Delta H_f^0 = -146.1 \pm 0.8$ Kcal/mole, which is in good agreement 
with the value found by Boyd, Cobble, and Smith.$^{20}$

Boyd, Cobble, and Smith$^{20}$ estimated the standard 
entropies for all three rhenium oxides at 298.16°K:
$S_{ReO_2}^0 = 44.0 \pm 3.6$ e.u., $S_{ReO_3}^0 = 19.8$ e.u., and $S_{ReO_2}^0 = 17.4$ e.u. They also estimated the standard heat of formation of ReO$_2$ to be $\Delta H_f^0 = -101.3$ Kcal/mole using oxidation 
potentials listed by Latimer$^{22}$ and the estimated value of $S_{ReO_2}^0$. By using the estimated entropy and measured heat of 
formation of Re$_2$O$_7$, the standard free energy of formation 
of Re$_2$O$_7$ at 298.16°K was calculated to be -258.7 Kcal/mole 
by Boyd, Cobble, and Smith.$^{20}$ Busey$^{18}$ used his measured 
entropy value and an average heat of formation of -296.7 
Kcal/mole to calculate a free energy of formation for 
Re$_2$O$_7$, $\Delta F^0_{298.16} = -255.0 \pm 2$ Kcal/mole.

King and Cobble$^{21}$ estimated the standard entropy of 
ReO$_3$, $S_{298.16}^0 = 19.3 \pm 2.5$ e.u. and used this with their 
value of the standard heat of formation to calculate the 
standard free energy of formation, $\Delta F^0_{298.16} = -128.1 \pm 0.8$ 
Kcal/mole.

Brewer$^{23}$ listed some estimates of the thermodynamic 
properties of the rhenium oxides, including a melting point 
of 160°C for ReO$_3$. Coughlin$^{24}$ estimated a heat of fusion 
and the high temperature heat content for ReO$_3$ and, based on
the data given by Brewer\textsuperscript{23} and $S_{298.16}^0 = 10.0$ e.u. for rhenium as given by Rossini et al.,\textsuperscript{25} Coughlin\textsuperscript{24} published $\Delta H^0$ and $\Delta F^0$ values for ReO\textsubscript{3} (c, l) and Re\textsubscript{2}O\textsubscript{7} (c, l, g). Using the data of Ogawa\textsuperscript{6} and estimates of the entropy and heat content, $\Delta H^0$ and $\Delta F^0$ values were published for Re\textsubscript{2}O\textsubscript{8} by Coughlin.\textsuperscript{24}

The vapor pressure of Re\textsubscript{2}O\textsubscript{7} has been measured by Ogawa\textsuperscript{6} and by Smith, Line, and Bell.\textsuperscript{26} Although Smith, Line, and Bell\textsuperscript{26} exerted much better control over the temperature in their experiments, there are only minor differences between their data and those of Ogawa.\textsuperscript{6} Ogawa\textsuperscript{6} found the melting point and the boiling point of Re\textsubscript{2}O\textsubscript{7} to be 296°C and 362.5°C, respectively, and from log $P$ versus inverse temperature plots, the heat of fusion and heat of evaporation were determined to be $15.34$ Kcal/mole and $18.06$ Kcal/mole, respectively. The melting and boiling points determined by Smith, Line, and Bell\textsuperscript{26} were $300.3 \pm 0.3°C$ and $360.3 \pm 0.3°C$, respectively, while the heat of fusion and the heat of evaporation were $15.81 \pm 0.1$ Kcal/mole and $17.7 \pm 0.1$ Kcal/mole, respectively.

Deev and Smirnov\textsuperscript{27} measured the vapor pressure of ReO\textsubscript{2} and of ReO\textsubscript{3} by effusion techniques. The following equations were found to hold in the temperature ranges indicated:

\begin{align*}
\text{ReO}_2: \quad \log P(\text{mm Hg}) &= -14347/T + 11.65 \quad (650^\circ - 785^\circ C) \\
\text{ReO}_3: \quad \log P(\text{mm Hg}) &= -10882/T + 15.16 \quad (325^\circ - 420^\circ C).
\end{align*}
From these equations vapor pressures of 760 mm Hg are reached at 1363°C for ReO₂ and 614°C for ReO₃.

The vapor pressures of ReO₂ and ReO₃ were also measured by Budon and Tseft who used a jet stream or transpiration method. Their equations for the vapor pressures of ReO₂ and ReO₃ are shown below.

\[
\begin{align*}
\text{ReO}_2 : \log P(\text{mm Hg}) &= -4742/T + 5.345 \quad (300°-480°C) \\
\text{ReO}_3 : \log P(\text{mm Hg}) &= -4966/T + 7.745 \quad (480°-660°C).
\end{align*}
\]

The vapor pressure measurements on ReO₂ and ReO₃ should be considered with skepticism since no evidence has shown that either ReO₂ or ReO₃ exists as gaseous species. Lebedev suggests that ReO₂ breaks up into rhenium and gaseous Re₂O₇ on heating above 750°C in a vacuum and that above 440°C the vapor pressure of ReO₃ is difficult to determine because of the reaction

\[
3\text{ReO}_3(c) = \text{ReO}_2(c) + \text{Re}_2\text{O}_7(g).
\]

The decomposition of ReO₃ was studied by Deschanvres who found that the reaction proceeded according to

\[
8\text{ReO}_3(c) = 4\text{ReO}_2(c) + 2\text{Re}_2\text{O}_7(g) + O_2(g),
\]

using chemical analysis of the residue. The disproportionation reactions of ReO₂ and ReO₃ leaving layers of lower oxygen content phases on the surfaces of the parent particles would make it difficult to determine equilibrium partial pressures of the rhenium oxides in the gas phase.
This may have caused the considerable difference in the vapor pressures measured by Deev and Smirnov\textsuperscript{27} and by Budon and Tseft.\textsuperscript{28}

**Experimental Procedure**

The experimental phase of this investigation consisted of three parts. The first, the most important, was a quantitative determination of the free energy of formation of rhenium dioxide. The other two parts were qualitative experiments designed to check information in literature. The first of these was an attempt to determine the melting point of rhenium trioxide, and the second was a survey of the stability of rhenium dioxide at high temperatures in inert atmospheres and in moist atmospheres.

**Free energy of formation of rhenium dioxide**

The free energy of formation of rhenium dioxide was determined by a solid-electrolyte, galvanic cell technique. This technique, which employs $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ as the electrolyte, was introduced by Kiukkola and Wagner,\textsuperscript{29,30} who, along with Kingery et al.,\textsuperscript{31} Schmalzried,\textsuperscript{32} and Rapp,\textsuperscript{33} demonstrated that this method is excellent for determining differences in the partial molar free energies of oxygen of the electrodes.

The cells had Re-ReO\textsubscript{2} electrodes on one side and a reference electrode of either Ni-NiO or Cu-Cu\textsubscript{2}O on the
other side. The cells can be represented schematically as shown

\[
\text{Pt} \mid \text{Ni, NiO} \mid \text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85} \mid \text{Re, ReO}_2 \mid \text{Pt},
\]

and

\[
\text{Pt} \mid \text{Re, ReO}_2 \mid \text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85} \mid \text{Cu, Cu}_2\text{O} \mid \text{Pt}.
\]

The cell reactions for the cells as shown are

\[
\text{ReO}_2(c) + 2\text{Ni}(c) = \text{Re}(c) + 2\text{NiO}(c),
\]

and

\[
2\text{Cu}_2\text{O}(c) + \text{Re}(c) = \text{ReO}_2(c) + 4\text{Cu}(c).
\]

The reactions are written according to the convention that the electrode on the left of the cell as shown in the schematic diagram is negative when a positive current passes from left to right through the cell, and the electromotive force of the cell is then taken as positive.

The electromotive force or emf of the cell is measured as a function of temperature for each cell. The emf is then used to derive the free energy of formation of ReO\(_2\) by using the method described in the section on results.

A schematic diagram of the apparatus is shown in Figure 1.

The cell consisted of an H-form crucible of \(\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}\) similar to that described by Rapp, electrodes of Re-ReO\(_2\) and Ni-NiO (or Cu-Cu\(_2\)O), and platinum leads. The \(\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}\) was made from zirconyl
Figure 1. Schematic diagram of the galvanic cell apparatus.
nitrate solution and calcium carbonate using a method similar to that described by Kiukkola and Wagner. The calcium carbonate was dissolved in dilute nitric acid and mixed with the zirconyl nitrate solution. The mixture was then evaporated to dryness and decomposed by using a porcelain evaporating dish heated by a Fisher burner. The solid material was then crushed and ground and fired at 1500°C for 20 hours in a platinum crucible. The aggregate was then crushed and ground to a fine powder. The powder was then mixed with glycerine which acted as a binder while the powder was compacted into cylinders 5/8 inch in diameter by about 1/2 inch high using a steel die and pressures of about 20,000 psi. The cylinders were scraped clean on the outside and fired at 1200°C for 20 hours on a platinum plate. A high speed, dental drill was then used to cut cavities in each end of the cylinder so that an H-form crucible resulted. The crucibles were then fired in a gas-oxygen furnace at approximately 2100°C for 3 to 4 hours. The crucibles shrunk about 15% and distorted slightly during the final firing. The Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ was quite dense but it could be ground by using silicon carbide paper. The ends of the crucibles were ground flat so that good contact with a platinum foil cover could be achieved. X-ray diffraction patterns obtained on powder ground from the crucibles fired at 2100°C showed the Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ to be in the fluorite phase, the same as
that found by Kingery et al. and Schmalzried. Traces of peaks which could be attributed to CaZrO$_3$ were also found. Chemical analyses of starting materials are given in Table 3.

The electrodes consisted of approximately one to one by volume mixtures of the appropriate metal and oxide powders which were compacted into the ends of the H-form crucible. The powders were held in place during the assembly of the cell by platinum foil covers which also acted as the cell leads. The metal and oxide powders used in the electrodes had been heated to at least 500°C for several hours and then stored in a desiccator prior to being used. Each oxide was made from the appropriate metal powder. Both NiO and Cu$_2$O were made by heating Ni and Cu in an alumina boat in air to about 1000°C. The ReO$_2$ was made from ReO$_3$ and Re by reacting them in a vycor capsule at 800°C for 24 hours. The ReO$_3$ was made from Re by the method described by Andrieth. 

The identity of the phases in each electrode was checked before and after each experiment by using X-ray diffraction. A General Electric XRD-5 diffractometer with Cu K$_\alpha$ radiation and a Norelco 57.3mm powder camera with Mo K$_\alpha$ radiation were both used to obtain diffraction patterns. No changes in phase were ever noted and except in one case mentioned later, no relative changes in peak intensity were observed.
Table 3
Chemical Analyses of Starting Materials

<table>
<thead>
<tr>
<th>Material, Source</th>
<th>Reported Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconyl Nitrate Solution, National Lead Co.</td>
<td>As$_2$O$_3$ 1 ppm max.</td>
</tr>
<tr>
<td></td>
<td>Cu 4 ppm max.</td>
</tr>
<tr>
<td></td>
<td>Fe 35 ppm max.</td>
</tr>
<tr>
<td></td>
<td>Hf 200 ppm max.</td>
</tr>
<tr>
<td></td>
<td>Pb 10 ppm max.</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$ 20%</td>
</tr>
<tr>
<td>Calcium Carbonate Powder, Mallinckrodt Chemical Works</td>
<td>Ba &lt; 0.005 %</td>
</tr>
<tr>
<td></td>
<td>Cl &lt; 0.001 %</td>
</tr>
<tr>
<td></td>
<td>Fe &lt; 0.0015%</td>
</tr>
<tr>
<td></td>
<td>Pb &lt; 0.0005%</td>
</tr>
<tr>
<td></td>
<td>Mg &lt; 0.02 %</td>
</tr>
<tr>
<td></td>
<td>NH$_4$ &lt; 0.003 %</td>
</tr>
<tr>
<td></td>
<td>NO$_3$ &lt; 0.005 %</td>
</tr>
<tr>
<td></td>
<td>PO$_4$ &lt; 0.001 %</td>
</tr>
<tr>
<td></td>
<td>K &lt; 0.005 %</td>
</tr>
<tr>
<td></td>
<td>Na 0.05 %</td>
</tr>
<tr>
<td></td>
<td>Sr 0.02 %</td>
</tr>
<tr>
<td></td>
<td>SO$_4^2$ &lt; 0.005 %</td>
</tr>
<tr>
<td>Rhenium Powder, Chase Brass and Copper Co.</td>
<td>Al &lt; 1 ppm</td>
</tr>
<tr>
<td></td>
<td>Ca &lt; 1 ppm</td>
</tr>
<tr>
<td></td>
<td>Cu &lt; 1 ppm</td>
</tr>
<tr>
<td></td>
<td>Fe 10 ppm</td>
</tr>
<tr>
<td></td>
<td>Mg &lt; 1 ppm</td>
</tr>
<tr>
<td></td>
<td>Mo 35 ppm</td>
</tr>
<tr>
<td></td>
<td>K &lt; 0.0002%</td>
</tr>
<tr>
<td></td>
<td>Si &lt; 1 ppm</td>
</tr>
<tr>
<td></td>
<td>W &lt; 1 ppm</td>
</tr>
<tr>
<td>Copper Powder, J. T. Baker Chemical Co.</td>
<td>no analysis available,</td>
</tr>
<tr>
<td></td>
<td>listed as &quot;purified</td>
</tr>
<tr>
<td></td>
<td>copper powder&quot;</td>
</tr>
<tr>
<td>Nickel Powder, International Nickel Co.</td>
<td>Al &lt; 0.002%</td>
</tr>
<tr>
<td></td>
<td>C 0.06 %</td>
</tr>
<tr>
<td></td>
<td>Co &lt; 0.01 %</td>
</tr>
<tr>
<td></td>
<td>Cu &lt; 0.001%</td>
</tr>
<tr>
<td></td>
<td>Fe &lt; 0.01 %</td>
</tr>
<tr>
<td></td>
<td>Mo &lt; 0.002%</td>
</tr>
<tr>
<td></td>
<td>Mn &lt; 0.004%</td>
</tr>
<tr>
<td></td>
<td>O 0.128%</td>
</tr>
<tr>
<td></td>
<td>P &lt; 0.001%</td>
</tr>
<tr>
<td></td>
<td>Si &lt; 0.005%</td>
</tr>
<tr>
<td></td>
<td>S &lt; 10 ppm</td>
</tr>
<tr>
<td></td>
<td>Ti &lt; 0.005%</td>
</tr>
<tr>
<td></td>
<td>Zr &lt; 0.005%</td>
</tr>
</tbody>
</table>
Table 3 (continued)

<table>
<thead>
<tr>
<th>Material, Source</th>
<th>Reported Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Bar, Battelle Memorial Institute</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td></td>
<td>Be</td>
</tr>
<tr>
<td></td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>Co</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td></td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>Sb, As, Ca, Cd, Pb, Mo, Sn, Ti, W, Zn, V, Zr not detected</td>
</tr>
<tr>
<td>Molybdenum Powder, Fansteel Metallurgical Corp.</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
</tr>
</tbody>
</table>

The furnace was constructed by the Marshall Products Company, and the furnace temperature was controlled to at least ±0.5°C by a Honeywell controller-recorder. Argon that had been passed over hot titanium chips was forced through the furnace chamber for several hours prior to beginning an experiment and then during the experiment.

Each experiment began with the furnace at room temperature. Several hours were required to reach the temperature range where a cell emf could be observed. Measurements were then taken at constant temperature until the emf
was constant and reversible (see below). The temperature would then be changed and the process repeated.

The temperature of the cell was determined by using a Pt-10%Rh thermocouple which had been calibrated at the melting points of gold and silver by the wire method. The thermocouple emf was measured to $10^{-6}$ volts with a Rubicon potentiometer having an external battery, standard cell, and sensitive Honeywell galvanometer.

The emf of the cell was measured to $10^{-5}$ volts by a separate Rubicon potentiometer also with an external battery and standard cell, but with a less sensitive Honeywell galvanometer. The cell emf was opposed by an equal emf of the potentiometer except for very brief periods when the standard cell was used to adjust the potentiometer battery or when the cell emf was checked for reversibility.

The cells were tested for reversibility first by reading the emf, then unbalancing the potentiometer so that a small current passed in one direction for a period of about a minute, then rebalancing and reading the emf, then unbalancing in the opposite direction for a similar period, and finally by rebalancing the potentiometer and reading the emf. When the three emf values agreed within $10^{-4}$ volts the cell was assumed to be reversible.

The temperature range of this investigation was limited to $670^\circ$ to $850^\circ$C. Below $600^\circ$C the conductivity of the electrolyte is too small for practical use, and above $850^\circ$C
appreciable losses of ReO$_2$ were noted probably by the reaction

$$7\text{ReO}_2(c) = 3\text{Re}(c) + 2\text{Re}_2\text{O}_7(g).$$

These losses were observed by changes in the X-ray diffraction patterns of the Re-ReO$_2$ electrodes after experiments where the temperature was above 800°C and especially above 850°C. Some deposits of higher rhenium oxides were noted on the cold parts of the furnace chamber after the experiments at higher temperatures.

**Melting point of ReO$_3$**

An attempt was made to determine the melting point of ReO$_3$. ReO$_3$ powder made by the method of Audrieth$^{11}$ was compacted into a vycor tube that had been previously sealed at one end. The tube was purged several times with argon and a fore-pump and then sealed off with about one-third atmosphere argon present. A thermometer was attached to the capsule, and these were heated in a small oven. The character of the ReO$_3$ was checked at intervals of 5°C up to 506°C by withdrawing the specimen and rotating it while watching the contents. The thermometer was then replaced by a chromel-alumel thermocouple and heating and examination were continued up to 600°C. At temperatures of 500°C and higher yellow deposits could be formed on the inside of the capsule by holding the hot capsule with a large pair of pliers. The residues in capsules where yellow deposits had
been formed were X-rayed and found to contain both ReO$_2$ and ReO$_3$.

**Stability of ReO$_2$ in argon and argon-water vapor gas mixtures**

The second series of qualitative experiments involved exposing ReO$_2$ to dry argon and to argon with fixed partial pressures of water vapor. ReO$_2$ powder was placed in a Pt vessel which could be suspended from a balance in the combustion chamber of a furnace. Argon or argon with water vapor was passed through the chamber and the weight of the specimen was observed as a function of time. The apparatus was checked for leaks by suspending specimens of zone-refined iron and of tungsten in place of the Pt vessel. Neither the iron nor the tungsten gained weight during several hours of exposure to the argon. The ReO$_2$ specimens lost weight in a linear fashion under all conditions. The range of conditions involved temperatures of 609° to 947°C and gases from pure argon to greater than one-half atmosphere water vapor plus argon. The flow rate was also varied for certain temperature and gas mixture conditions. The residue left in the Pt vessel after each series of experiments was X-rayed and both Re and ReO$_2$ were present in each case.
Results

Free energy of formation of ReO$_2$

The interpretation of the electrolytic cell data is illustrated using the following example. For the cell

Pt $|$ Ni,Nio $|$ Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ $|$ Re,ReO$_2$ $|$ Pt

the reaction is formulated in terms of the transfer of two gram atoms of oxygen from the right side to the left side,

$$\text{ReO}_2(c) + 2\text{Ni}(c) = 2\text{NiO}(c) + \text{Re}(c).$$

The free energy change for this cell reaction, $\Delta F_{\text{cell}}$, is expressed as follows:

$$\Delta F_{\text{cell}} = F^0_{\text{O}_2,(\text{Ni,NiO})} - F^0_{\text{O}_2,(\text{Re,ReO}_2)}$$  \hspace{1cm} (1)

where $F^0_{\text{O}_2}$ is the partial molar free energy of oxygen. $F^0_{\text{O}_2}$ for each electrode may be expressed as

$$F^0_{\text{O}_2,(\text{Ni,NiO})} = F^0_{\text{O}_2} + RT \ln \alpha_{\text{O}_2,(\text{Ni,NiO})},$$  \hspace{1cm} (2)

and

$$F^0_{\text{O}_2,(\text{Re,ReO}_2)} = F^0_{\text{O}_2} + RT \ln \alpha_{\text{O}_2,(\text{Re,ReO}_2)},$$  \hspace{1cm} (2a)

where $F^0_{\text{O}_2}$ is the standard molar free energy of oxygen and $\alpha_{\text{O}_2}$ is the activity of oxygen. The standard state for oxygen is that state in which the fugacity of oxygen is equal to one for the temperature under consideration. The equilibrium constants for the reaction

$$2\text{Ni}(c) + \text{O}_2(g) = 2\text{NiO}(c),$$
and
\[ \text{Re}(c) + O_2(g) = \text{ReO}_2(c) \]

are given by
\[ K_{\text{Ni}} = \frac{\alpha_{\text{NiO}}^2}{\alpha_{\text{Ni}}^2 \alpha_{O_2}^0, (\text{Ni},\text{NiO})} \quad (3) \]

and
\[ K_{\text{Re}} = \frac{\alpha_{\text{ReO}_2}}{\alpha_{\text{Re}} \alpha_{O_2}^0, (\text{Re},\text{ReO}_2)} \quad (3a) \]

where the activity of each solid is indicated by the superscript. The standard states chosen for Ni and Re are the metals saturated with their oxides at one atmosphere total pressure at the temperature under consideration. The standard states chosen for NiO and ReO\(_2\) are the oxides saturated with their metals at one atmosphere total pressure at the temperature under consideration. It is assumed that each solid was in its standard state in the experimental environment of this investigation, and, thus, the activity of each solid is unity. Equations (3) and (3a) now reduce to
\[ K_{\text{Ni}} = \frac{1}{\alpha_{O_2}^0, (\text{Ni},\text{NiO})} \quad (3b) \]

and
\[ K_{\text{Re}} = \frac{1}{\alpha_{O_2}^0, (\text{Re},\text{ReO}_2)} \quad (3c) \]

By using the relationship between the standard free energy of reaction and the equilibrium constant,
\[ \Delta F^0 = -RT \ln K \quad (4) \]
and combining equations (2), (2a), (3b), and (3c) into equation (1) yields

\[ \Delta F_{\text{cell}} = 2 \Delta F_{\text{NiO}}^0 - \Delta F_{\text{ReO}_2}^0, \]  

(1a)

where \( \Delta F_{\text{NiO}}^0 \) and \( \Delta F_{\text{ReO}_2}^0 \) are the standard molar free energies of formation of the oxides.

The reversible emf of the cell is related to the free energy change of the reaction by

\[ \Delta F_{\text{cell}} = -4 F \mathcal{E}, \]  

(1b)

where \( \mathcal{E} \) is the cell emf and \( F \) is the Faraday constant.

Equation (1b) is valid if conduction in the electrolyte is essentially due to migration of oxygen ions, and electrochemical equilibrium is attained at all the interfaces.

Combining equations (1a) and (1b) and rearranging gives

\[ \Delta F_{\text{ReO}_2}^0 = 2 \Delta F_{\text{NiO}}^0 + 4 F \mathcal{E}. \]  

(5)

Similarly for the other cells used

\[ \Delta F_{\text{ReO}_2}^0 = 2 \Delta F_{\text{Cu}_2O}^0 - 4 F \mathcal{E}. \]  

(6)

These are the equations used to evaluate the electrolytic cell data. The unknown, \( \Delta F_{\text{ReO}_2}^0 \), is given in terms of a known quantity, either \( \Delta F_{\text{NiO}}^0 \) or \( \Delta F_{\text{Cu}_2O}^0 \), and an experimentally determined quantity.

The values of \( \Delta F_{\text{NiO}}^0 \) and \( \Delta F_{\text{Cu}_2O}^0 \) are taken from the literature and in each case an equation linear with temperature was used. These equations are
$$\Delta F^0_{\text{NiO}} = -56000 + 20.3T$$  \hspace{1cm} (7)

and

$$\Delta F^0_{\text{Cu}_2\text{O}} = -39980 + 17.05T$$  \hspace{1cm} (8)

Equation (7) was recommended by Chipman, and it reproduces the values found by Kiukkola and Wagner and by Rapp to within ±100 cal. In the studies by Kiukkola and Wagner and by Rapp electrolytic cells were used employing the well defined iron-wüstite equilibrium as a reference. Equation (8) is based on the work of Bidwell, who is the only investigator of the Cu-Cu$_2$O equilibrium at temperatures below 800°C.

The reference standard molar free energy values have been taken from investigations where electrolytic cells were used, even though these values are not always in agreement with the values determined by calorimetric methods. High temperature free energies determined by equilibrium experiments are considered to be more accurate than "third law" calculations by using calorimetric data.

Two separate runs were made with each of the cells used. Several reversible emfs were found at different temperatures in each run. The results are summarized in Table 4 which gives the reference electrode, temperature, emf, and calculated $\Delta F^0_{\text{ReO}_2}$.

The $\Delta F^0_{\text{ReO}_2}$ data were considered to be in two sets, one for the Cu-Cu$_2$O reference electrode and one for the Ni-NiO reference electrode. Each set of $\Delta F^0_{\text{ReO}_2}$ versus
Table 4
Free Energy of Formation of ReO$_2$ Data

<table>
<thead>
<tr>
<th>Reference Electrode</th>
<th>Temperature °K</th>
<th>emf volts</th>
<th>$-\Delta F^\circ_{\text{ReO}_2}$ cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cu$_2$O</td>
<td>963.5</td>
<td>0.1784</td>
<td>63,450</td>
</tr>
<tr>
<td></td>
<td>996.9</td>
<td>0.1748</td>
<td>62,070</td>
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<tr>
<td></td>
<td>999.7</td>
<td>0.1753</td>
<td>62,060</td>
</tr>
<tr>
<td></td>
<td>1022.4</td>
<td>0.1722</td>
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<td>1040.2</td>
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<td>1049.7</td>
<td>0.1740</td>
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<td>1060.6</td>
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<td>1060.7</td>
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<td>1100.8</td>
<td>0.1672</td>
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<tr>
<td>Ni-NiO</td>
<td>945.5</td>
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<td>64,840</td>
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<tr>
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<td>951.0</td>
<td>0.0947</td>
<td>64,650</td>
</tr>
<tr>
<td></td>
<td>968.1</td>
<td>0.0944</td>
<td>64,000</td>
</tr>
<tr>
<td></td>
<td>970.3</td>
<td>0.0964</td>
<td>63,720</td>
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<td></td>
<td>972.0</td>
<td>0.0968</td>
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<td></td>
<td>973.5</td>
<td>0.0989</td>
<td>63,350</td>
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<tr>
<td></td>
<td>993.9</td>
<td>0.1019</td>
<td>62,250</td>
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<td></td>
<td>996.2</td>
<td>0.1048</td>
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<td>1028.6</td>
<td>0.1056</td>
<td>60,500</td>
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<td>1030.4</td>
<td>0.1075</td>
<td>60,250</td>
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<tr>
<td></td>
<td>1057.4</td>
<td>0.1093</td>
<td>58,970</td>
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<td></td>
<td>1095.5</td>
<td>0.0950</td>
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</tr>
<tr>
<td></td>
<td>1103.2</td>
<td>0.0951</td>
<td>58,450</td>
</tr>
<tr>
<td></td>
<td>1107.3</td>
<td>0.0955</td>
<td>58,230</td>
</tr>
</tbody>
</table>
temperature data was treated by the least squares method. The resulting equations are

for Cu-Cu$_2$O: \[ \Delta F^\circ_{\text{ReO}_2} = -101560 + 39.59T \] (9)

and

for Ni-NiO: \[ \Delta F^\circ_{\text{ReO}_2} = -103930 + 41.68T \] . (10)

The differences between the \( \Delta F^\circ_{\text{ReO}_2} \) values calculated by each equation are 280 and 90 cal/mole at 1000° and 1100°K, respectively. The \( \Delta F^\circ_{\text{ReO}_2} \) values calculated from the experimental data and the least squares equations are shown in Figure 2.

The standard deviations in the reversible emf values were equal to or less than 0.0008 volt at each temperature. This contributes an error of about ±100 cal to the \( \Delta F^\circ_{\text{ReO}_2} \) values. When this error is combined with estimated errors in the free energy values for the reference electrodes, a probable error of ±300 cal is assigned to the \( \Delta F^\circ_{\text{ReO}_2} \) values given in Table 4. The rather large difference in the temperature coefficients in equations (9) and (10) may be attributed to scatter in the data and the relatively small temperature intervals used in this investigation. Account of the difference must be taken when extrapolating the equations for \( \Delta F^\circ_{\text{ReO}_2} \) beyond the temperature range of this investigation.
Figure 2. Experimental $\Delta F^\circ_{\text{ReO}_2}$ values versus temperature.
Melting point of ReO₂

No indication of melting of ReO₂ was noted in the experiments, and it can be concluded that ReO₂ does not melt at temperatures up to 600°C. The formation of yellow deposits on the walls of capsules that were heated to above 500°C is evidence that ReO₂ partially decomposed. This decomposition was probably according to the reaction

\[ 3\text{ReO}_2(c) = \text{ReO}_2(c) + \text{Re}_2\text{O}_7(g), \]

since the presence of both ReO₂ and ReO₃ was indicated by X-ray diffraction analysis.

Stability of ReO₂ in argon and argon-water vapor gas mixtures

No correlation of the data from this set of experiments was possible. Since the specimen lost weight in all conditions and both Re and ReO₂ were present after each run, it is concluded that ReO₂ was decomposing according to the reaction

\[ 7\text{ReO}_2(c) = 3\text{Re}(c) + 2\text{Re}_2\text{O}_7(g). \]

When water vapor was present, it is likely that oxidation of Re and ReO₂ was occurring simultaneously with the decomposition of ReO₂.

Discussion

The free energy change is the most useful criterion for predicting relative stabilities in a multicomponent
system. The free energy changes for various reactions in the rhenium-oxygen system based on the data in the literature are shown in Figure 3. The $\Delta F^\circ$ values for ReO$_3$ and Re$_2$O$_7$ were taken from Coughlin,$^{24}$ and the free energy of formation of ReO$_2$ was calculated using the heat of formation and entropy of formation predicted by Boyd, Cobble, and Smith,$^{20}$ assuming $\Delta C_p = 0$ for the reaction

$$\text{Re}(c) + \text{O}_2(g) = \text{ReO}_2(c).$$

Consideration of several experimentally observable facts about the rhenium-oxygen system will illustrate that the data taken from the literature are unsatisfactory, especially at high temperatures. The most obvious discrepancy is that the data predict that Re$_2$O$_7$ is unstable with respect to the formation of ReO$_3$ in one atmosphere of oxygen. This is contrary to the experience of all investigators reporting on the formation of Re$_2$O$_7$. A peritectic reaction is predicted at 780°C involving Re, ReO$_2$, and ReO$_3$ according to

$$3\text{ReO}_2(c) = \text{Re}(c) + 2\text{ReO}_3(l).$$

If this reaction actually took place, ReO$_2$ would not be found at temperatures above 780°C. Magneli$^{10}$ found ReO$_2$ to be stable to 1050°C and obtained ReO$_2$ by reacting Re and ReO$_3$ at 800°C. The stability of ReO$_2$ at temperatures above 780°C is demonstrated in the works of Tribalat, Jungfleisch, and Collet,$^8$ Deschanvres,$^9$ and this author.
Figure 3. Standard free energy changes for the reactions

\[ \frac{2y}{z-xy} \text{ReO}_x + \text{O}_2 = \frac{2}{z-xy} \text{Re}_y\text{O}_z \]

based on data in the literature.
Equilibrium vapor pressures of Re\(_2\)O\(_7\)(g) can be calculated for the reactions

\[ 7\text{ReO}_2(c) = 3\text{Re}(c) + 2\text{Re}_2\text{O}_7(g) \]

and

\[ 3\text{ReO}_3(l) = \text{ReO}_2(c) + \text{Re}_2\text{O}_7(g) \]

using the literature data. The predicted values are \((10)^{-8}\) atm or lower for temperatures below 1000\(^\circ\)K, yet the above reactions are known to occur. Lebedev\(^2\) reports that in vacuo the first reaction occurs above 750\(^\circ\)C and the second reaction occurs above 440\(^\circ\)C.

It is obvious that a revision of the free energy of formation data is in order for all the rhenium oxides.

**Free energy of formation of ReO\(_2\)**

The data on ReO\(_2\) obtained in this investigation are considered to be accurate to within \(\pm 300\) cal in the temperature interval investigated. An average of the least squares equations, (9) and (10), for \(\Delta F^\circ_{\text{ReO}_2}\) yields the following equation:

\[ \Delta F^\circ_{\text{ReO}_2} = -102750 + 40.67T (\pm 300), \text{ cal/mole.} \quad (11) \]

This equation gives \(\Delta F^\circ_{\text{ReO}_2}\) values about 1350 cal more negative than the equation formulated from the predictions of Boyd, Cobble, and Smith.\(^{20}\) The differences are surprisingly small considering that Boyd, Cobble, and Smith\(^{20}\) were making an estimate and assigned a probable error of \(\pm 3000\) cal to their values.
Although an equation linear with temperature fits the data of this investigation quite well, it is best to include additional terms for the change in heat capacity, $\Delta C_p$, in the free energy equation. This allows the equation to be used over a greater temperature range with increased confidence. The change in heat capacity was estimated since there are no heat capacity data for ReO$_2$. The heat capacity of ReO$_2$ was assumed to be equal to that of WO$_2$. This assumption is based on the nearly equal molecular weights of WO$_2$ and ReO$_2$ and the similarity of their crystal structures. The latter has been plotted out by Magneli and Marinder.$^{15}$ The heat capacity of WO$_2$ is given by King, Weller, and Christensen,$^{36}$ and it was rounded off to

$$C_p = 15.5 + 3.6 \times 10^{-3} T - 2.8 \times 10^{-5} T^{-2}, \text{ cal/mole/}^\circ\text{K}, \quad (12)$$

for ReO$_2$. The heat capacities of oxygen and rhenium are given by K. K. Kelley,$^{17}$

for O$_2$:  

$$C_p = 7.16 + 1.0 \times 10^{-3} T - 0.40 \times 10^{-5} T^{-2}, \text{ cal/mole/}^\circ\text{K}, \quad (13)$$

and

for Re:  

$$C_p = 5.66 + 1.3 \times 10^{-3} T, \text{ cal/mole/}^\circ\text{K} \quad (14)$$

The equation for $C_p, \text{Re}$ was corrected to fit the data of Smith, Oliver, and Cobble$^{16}$ by adding to the constant term to give
\[ C_{p,Re} = 5.76 + 1.3(10)^{-3}T, \text{ cal/mole/}^\circ\text{K} \]  \hspace{1cm} (15)

The temperature coefficient and the constant term in the free energy equation taken from the data are assumed to be equal to the standard entropy of formation and standard heat of formation, respectively, at the average temperature of this investigation, 1025°K. The standard heat of formation, standard entropy of formation, and standard free energy of formation at any temperature, \( T \), may now be calculated by using the following equations:

\[ \Delta H^0_T = \Delta H^0_{1025} + \int_{1025}^{T} \Delta C_p \, dT, \]  \hspace{1cm} (16)

\[ \Delta S^0_T = \Delta S^0_{1025} + \int_{1025}^{T} \frac{\Delta C_p}{T} \, dT, \]  \hspace{1cm} (17)

and

\[ \Delta F^0_T = \Delta H^0_T - T \Delta S^0_T. \]  \hspace{1cm} (18)

These equations are valid only if there are no phase changes. The polymorphism of ReO\(_2\) was noted by Magneli,\(^{10}\) but it is unlikely that the monoclinic to orthorhombic crystal structure change involved would have an appreciable heat effect. In the following equations it is assumed that no important phase changes take place. Substituting equations (12), (13), and (15) into equation (16) and integrating yields.

\[ \Delta H^0_T = -106310 + 2.58T + 0.65(10)^{-3}T^2 + 2.4(10)^{5.5}T^{-1}. \]  \hspace{1cm} (19)

Similarly for equations (17) and (18) the following equations are derived:

\[ \Delta S^0_T = -59.97 + 5.94 \log T + 1.3(10)^{-3}T + 1.2(10)^{5}T^{-2}, \]  \hspace{1cm} (20)
and

\[ \Delta F^o_T = -106310 + 62.55T - 5.94T\log T - 0.65(10)^{-3}T^2 + 1.2(10)^{5}T^{-1}. \]  

Equation (21) gives values of \( \Delta F^o_{\text{ReO}_2} \) equal to within 30 cal to those calculated by equation (11) in the temperature interval from 940° to 1110°K.

As a check on the assumption that the heat capacity of ReO₂ is equal to that of WO₂, the standard entropies can be compared since they also should be equal. \( S^o_{\text{ReO}_2} \) values were calculated by using equation (20) and appropriate values of \( S^o_{\text{Re}} \) and \( S^o_{\text{O}_2} \). The entropy values are compared in Table 5.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>( S^o_{\text{ReO}_2} ) (e.u.)</th>
<th>( S^o_{\text{WO}_2} ) (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.16</td>
<td>12.37</td>
<td>12.08</td>
</tr>
<tr>
<td>1000</td>
<td>34.26</td>
<td>31.99</td>
</tr>
</tbody>
</table>

The difference between the standard entropy values for WO₂ and those calculated for ReO₂ is small, and this gives added support to the assumption of equal heat capacities.

**Free energy of formation of ReO₃**

The standard heat of formation is the only thermodynamic quantity that has been experimentally determined for ReO₃. Boyd, Cobble, and Smith²⁰ found \( \Delta H^o_{298.16} = \)
\(-146.1 \pm 3.0\) Kcal/mole using combustion calorimetry, while King and Cobble\(^2\) found \(\Delta H^0_{298.16} = -146.1 \pm 0.8\) Kcal/mole using measurements of the \(\text{ReO}_2/\text{ReO}_4^-\) electrode potential. A value of \(\Delta H^0_{298.16} = -146.1 \pm 3.0\) Kcal/mole is assumed to be valid for these calculations.

In order to calculate the free energy function, estimates of the heat capacity and entropy of \(\text{ReO}_3\) must be made. The standard entropy of \(\text{ReO}_3\), \(S^0_{298.16}\) was estimated by Boyd, Cobble, and Smith\(^2\) to be \(19.8\) e.u. and by King and Cobble\(^2\) to be \(19.3 \pm 2.5\) e.u. For these calculations the heat capacity and entropy of \(\text{ReO}_3\) are assumed to be equal to that of \(\text{WO}_3\). The molecular weights and crystal structures of \(\text{ReO}_3\) and \(\text{WO}_3\) are both very similar, and these similarities are the basis for the assumption. This assumption leads to \(S^0_{298.16} = 18.20\) and

\[
C_P,\text{ReO}_3 = 21.3 + 3.4(10^{-3})T - 4.4(10^5)T^{-2}\text{ cal/mole/°K} \quad (22)
\]

Combining this equation with \(3/2\) times equation (13) and equation (15) yields the following:

\[
\Delta C_p = 4.8 + 0.6(10^{-3})T - 3.8(10^5)T^{-2}\text{ cal/mole/°K} \quad (23)
\]

The standard entropy of formation for \(\text{ReO}_3\) is estimated to be \(\Delta S^0_{298.16} = -64.2\) e.u.

The standard heat and entropy of formation may now be calculated by using equations (16) and (17) by changing the reference temperature from \(1025°K\) to \(298.16°K\). Integration of the appropriate equation yields
\[ \Delta H_T^0 = -148840 + 4.8T + 0.3(10)^{-3}T^2 + 3.8(10)^5T^{-1}, \]

and

\[ \Delta S_T^0 = -93.9 + 11.05 \log T + 0.6(10)^{-3}T + 1.9(10)^3T^{-2}. \]

Combining equations (24) and (25) with equation (18) yields the free energy equation,

\[ \Delta F_T^0 = -148840 + 98.7T - 11.05 T \log T - 0.3(10)^{-3}T^2 + 1.9(10)^5T^{-1}. \]

It is assumed that no phase transformations occur in ReO_3 in the calculations of \( \Delta H_T^0 \), \( \Delta S_T^0 \), and \( \Delta F_T^0 \).

**Free energy of formation of Re_2O_7**

The thermodynamic data available for Re_2O_7 are extensive, with high temperature heat capacity the only information missing. The standard entropy, the heat capacity, and the average heat of formation at 298.16°C given by Busey are used in the following calculations, along with the melting and boiling points and heats of fusion and evaporation determined by Smith, Line, and Bell.

The heat capacity of Re_2O_7 was extrapolated to the melting point using the value determined by Busey at 298.16°C, \( C_p,_{Re_2O_7} = 39.73 \), and assuming a value of \( C_p = 7 \text{ cal/g-atom/°K} \) at the melting point. This practice is recommended by K. K. Kelley and by Kubaschewski and Evans, except that the latter recommend a value of 7.25 cal/g-atom/°K at the first phase transition temperature. A heat
capacity equation linear with temperature was derived

\[ C_{p,\text{Re}_2\text{O}_7} = 14.50 + 84.6(10)^{-3}T, \text{cal/mole}/^{°}\text{K} \, . \quad (27) \]

Equation (27) combined with equations (13) and (15) gives the change in heat capacity for the reaction

\[ 2\text{Re}(c) + \frac{1}{2}\text{O}_2(g) = \text{Re}_2\text{O}_7(c) , \]

\[ \Delta C_p = -22.10 + 78.5(10)^{-3}T + 1.4(10)^{-5}T^2 \text{cal/mole}/^{°}\text{K}. \, (28) \]

The standard heat and entropy of formation up to 573.5°K may now be calculated by using the equations

\[ \Delta H^\circ_T = -296700 + \int_{298.16}^{T} \frac{\Delta C_p}{298.16} dT , \quad (29) \]

and

\[ \Delta S^\circ_T = -139.78 + \int_{298.16}^{T} \frac{\Delta C_p}{T} dT . \quad (30) \]

These equations yield on integration

\[ \Delta H^\circ_T = -293130 - 22.1T + 39.25(10)^{-3}T^2 - 1.4(10)^{-5}T^{-1} , \quad (31) \]

and

\[ \Delta S^\circ_T = -36.50 - 50.89 \log{T} + 78.5(10)^{-3}T - 0.7(10)^{-5}T^{-2} . \quad (32) \]

Substitution of equations (31) and (32) into equation (18) gives the free energy equation

\[ \Delta F^\circ_T = -293130 + 14.4T + 50.89T \log{T} - 39.25(10)^{-3}T^2 - 0.7(10)^{-5}T^{-1} . \quad (33) \]

At temperatures between 573.5 and 633.5°K Re\(_2\)O\(_7\) is in the liquid state. The heat capacity of liquid Re\(_2\)O\(_7\) is
assumed to be 63 cal/mole/°K throughout the liquid range. Combining this value with the heat capacities of oxygen and rhenium gives

\[ \Delta C_p = 26.4 - 6.1(10)^{-5}T. \]  \hspace{1cm} (34)

The \(T^{-2}\) term has been dropped since it makes a small contribution, and it is certainly less than the error in the estimated value of \(C_{p, Re_2O_7}\). The heat of fusion given by Smith, Line, and Bell is 15810 cal/mole. This gives an entropy of fusion of 27.60 e.u. Using a reference temperature of 573.5°K instead of 1025°K in equations (16) and (17) and adding appropriate terms for the heat and entropy of fusion gives upon integration

\[ \Delta H^0_T = -291520 + 26.43T - 3.05(10)^{-3}T^2, \]  \hspace{1cm} (35)

and

\[ \Delta S^0_T = -268.77 + 60.87 \log T - 6.1(10)^{-3}T. \]  \hspace{1cm} (36)

The values of \(\Delta H^0_{573.5}\) and \(\Delta S^0_{573.5}\) were calculated using equations (29) and (30). Combining equations (35) and (36) in equation (18) gives the free energy function for the temperature range 573.5 to 633.5°K

\[ \Delta F^0_T = -291520 + 295.2T - 60.87T\log T + 3.05(10)^{-3}T^2. \]  \hspace{1cm} (37)

Re\(_2O_7\) boils at 633.5°K. There are no data on gaseous Re\(_2O_7\) which would yield heat capacity information, and in this case a heat capacity change of zero is assumed for the reaction

\[ 2\text{Re}(c) + \frac{7}{2}\text{O}_2(g) = \text{Re}_2\text{O}_7(g). \]
The heat and entropy of evaporation given by Smith, Line, and Bell are $\Delta H_{\text{evap}} = 17700$ cal/mole, and $\Delta S_{\text{evap}} = 27.98$ e.u. By calculating $\Delta H^0_{633.5}$ and $\Delta S^0_{633.5}$ using equations (35) and (36) and adding the appropriate term for evaporation, the following equations are derived for temperatures above 633.5°K:

$$\Delta H^0_T = -258320 , \quad (38)$$

$$\Delta S^0_T = -74.07 , \quad (39)$$

and

$$\Delta F^0_T = -258320 + 74.07T . \quad (40)$$

A critical analysis of the free energy of formation equations derived for the rhenium oxides

By calculating the free energy change corresponding to several reactions, the validity of the free energy equations can be tested. From experimental observations the free energy change for the reaction

$$4\text{ReO}_3(c) + O_2(g) = 2\text{Re}_2O_7(c,l,g)$$

is known to be negative. The free energy change for this reaction was calculated using equations (26), (33), (37), and (40), and the results are shown in Table 6. Also shown in Table 6 are values of $\Delta F^0_T$ calculated using the equation

$$\Delta F^0_T = -145840 + 98.7T = 11.05T \log T - 0.3(10)^{-3}T^2 + 1.9(10^5T^{-1} . \quad (41)$$

It is obvious that equation (41) gives better values than equation (26) since the free energy change for the formation
Table 6
Free Energy Change for the Reaction
\[ 4\text{ReO}_3(c) + \text{O}_2(g) = 2\text{Re}_2\text{O}_7(c, l, g) \]

<table>
<thead>
<tr>
<th>( T(°K) )</th>
<th>( \Delta F^0_T ) using (26)</th>
<th>( \Delta F^0_T ) using (41)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.16</td>
<td>-3,510</td>
<td>-14,360</td>
</tr>
<tr>
<td>400</td>
<td>-1,300</td>
<td>-11,340</td>
</tr>
<tr>
<td>600</td>
<td>+ 320</td>
<td>- 8,120</td>
</tr>
<tr>
<td>800</td>
<td>-17,320</td>
<td>-24,360</td>
</tr>
<tr>
<td>1000</td>
<td>-36,220</td>
<td>-41,460</td>
</tr>
</tbody>
</table>

of Re\(_2\)O\(_7\) from ReO\(_3\) is negative at all temperatures. Equation (26) was modified to give equation (41) by adding 3000 cal to the \( \Delta H^0_{298.16} \) value. This is the limit of error assigned by Boyd, Cobble, and Smith.\(^{20}\)

The free energy change for the reaction
\[ 2\text{ReO}_3(c) + \text{Re}(c) = 3\text{Re}_2\text{O}_7(c) \]
calculated using equations (21) and (41) is -26000 cal at 800°K and -25600 cal at 1000°K. This is considered to be in satisfactory agreement with experimental observation since the reaction yielding ReO\(_2\) is known to take place.

The free energy changes for the reactions
\[ \frac{7}{2}\text{Re}_2\text{O}_7(c) = \frac{3}{2}\text{Re}(c) + \text{Re}_2\text{O}_7(g) \]
and
\[ 3\text{ReO}_3(c) = \text{ReO}_2(c) + \text{Re}_2\text{O}_7(g) \]
are given in Table 7 along with \( \Delta F \) values computed by correcting the data of Deev and Smirnov\(^{27}\) for Re\(_2\)O\(_7\) as the
**Table 7**

Free Energy Changes for the Reactions

I. \( \frac{7}{2} \text{ReO}_2(c) = \frac{3}{2} \text{Re}(c) + \text{Re}_2\text{O}_7(g) \),

II. \( 3\text{Re}_2\text{O}_3(c) = \text{ReO}_2(c) + \text{Re}_2\text{O}_7(g) \)

| Reaction | \( T(°K) \) | \( \Delta F^o_T \) | \( \Delta F^o_T \) (Deev and Smirnov)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>800</td>
<td>47,130</td>
<td>34,080</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>40,000</td>
<td>30,140</td>
</tr>
<tr>
<td>II.</td>
<td>700</td>
<td>14,870</td>
<td>10,950</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>8,130</td>
<td>5,400</td>
</tr>
</tbody>
</table>

Gaseous specie. The agreement is only fair for the first reaction, but it is good for the second reaction. Since the identity of the gaseous species over \( \text{ReO}_2 \) and \( \text{ReO}_3 \) has never been determined, the validity of the reaction involving formation of gaseous \( \text{Re}_2\text{O}_7 \) may be questioned. It is this author's opinion that these reactions do take place. The reaction proposed by Deschanvres

\[ 8\text{Re}_2\text{O}_3(c) = 4\text{ReO}_2(c) + 2\text{Re}_2\text{O}_7(g) + 0_2(g) \]

is not thermodynamically feasible since the equilibrium constant calculated from the equations given here predict \( \text{Re}_2\text{O}_7 \) pressures of \( 10^{-11} \) atmospheres at 700°K. Also, the oxygen pressure predicted by the reaction would be several orders of magnitude greater than that for equilibrium between \( \text{ReO}_2 \) and \( \text{ReO}_3 \).

The free energy of formation of \( \text{Re}_2\text{O}_7 \) given by equations (33), (37), and (40) are considered to be valid. The
probable errors vary from ±500 cal at 298.16°K to ±3000 cal for the liquid and gaseous Re₂O₇ regions. If the choice of heat capacity of solid Re₂O₇ at 573.5°K and for liquid Re₂O₇ were changed to 7.25 cal/mole/°K as suggested by Kubaschewski and Evans, the free energy values would be about 2500 cal more negative at high temperatures.

The free energy of formation of ReO₃ given by equation (41) is considered to be valid with a probable error of ±1000 cal at 298.16°K. The probable error would increase with temperature. Equation (41) is the least accurate since it includes estimations of the heat capacity and entropy throughout the entire temperature range.

The free energy of formation of ReO₂ given by equation (21) is considered to be valid with probable errors of ±300 cal at high temperatures increasing to ±1000 cal at low temperatures. The extrapolation from high temperatures using estimated heat capacity data and the rather large difference between the temperature coefficients in equations (9) and (10) cause the inverse error dependence.

The standard heat of formation of ReO₂ given by equation (19) is assumed to be valid, and equations (31), (35), and (38) are assumed to be valid for the standard heat of formation of Re₂O₇. The standard heat formation of ReO₃ is given by

\[ \Delta H^0_T = -145840 + 4.8T + 0.3(10)^{-3}T^2 + 3.8(10)^5T^{-1}, \] (42)
which resulted when equation (24) was modified to conform with equation (41).

The standard heats and free energies of formation of ReO$_2$, ReO$_3$, and Re$_2$O$_7$ calculated from the appropriate equations are given in Table 8.

Comparison of the data for ReO$_3$ and Re$_2$O$_7$ shown in Table 8 with the data for these oxides given by Coughlin$^{24}$ shows several large differences. The assumption that ReO$_3$ does not melt at temperatures below 1000°K causes the heat of formation to be several thousand cal more negative and the free energy of formation to be several thousand cal less negative than the values given by Coughlin.$^{24}$ The heat of formation values are practically the same for Re$_2$O$_7$, but the free energy values are up to 8250 cal more negative than those given by Coughlin.$^{24}$ At least part of this difference is due to the estimated value for the standard entropy of Re$_2$O$_7$ at 298.16°K of 40.0 e.u. used in the calculations of Coughlin.$^{24}$

A free energy versus temperature diagram for the rhenium-oxygen system is given in Figure 4. A comparison of Figure 4 with Figure 3 shows some very significant changes. Decomposition of ReO$_2$ is no longer predicted, while decomposition of ReO$_3$ to ReO$_2$ and gaseous Re$_2$O$_7$ is favored. At 882°K the Re$_2$O$_7$ partial pressure over ReO$_2$-ReO$_3$ mixtures reaches one atmosphere, and, thus, ReO$_3$ is not stable at one atmosphere total pressure above 882°K. Figure 5 is a
Table 8
Standard Heats and Free Energies of Formation of ReO\(_2\), ReO\(_3\), and Re\(_2\)O\(_7\)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Temperature (°K)</th>
<th>(-\Delta H^\circ_T) (cal/mole)</th>
<th>(-\Delta F^\circ_T) (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO(_2)(c)</td>
<td>298.16</td>
<td>104,680</td>
<td>91,700</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>104,570</td>
<td>87,560</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>104,380</td>
<td>82,980</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>104,150</td>
<td>78,900</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>103,840</td>
<td>74,490</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>103,530</td>
<td>70,340</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>103,200</td>
<td>66,190</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>102,840</td>
<td>62,120</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>102,470</td>
<td>58,090</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>102,080</td>
<td>54,040</td>
</tr>
<tr>
<td>ReO(_3)(c)</td>
<td>298.16</td>
<td>143,100</td>
<td>123,930</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>142,920</td>
<td>117,490</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>142,610</td>
<td>111,070</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>142,220</td>
<td>104,800</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>141,790</td>
<td>98,610</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>141,330</td>
<td>92,510</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>140,860</td>
<td>85,370</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>140,360</td>
<td>80,580</td>
</tr>
<tr>
<td>Re(_2)O(_7)(c)</td>
<td>298.16</td>
<td>296,670</td>
<td>255,010</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>296,040</td>
<td>240,850</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>294,650</td>
<td>227,190</td>
</tr>
<tr>
<td></td>
<td>573.5</td>
<td>293,170</td>
<td>217,460</td>
</tr>
<tr>
<td>Re(_2)O(_7)(l)</td>
<td>573.5</td>
<td>277,380</td>
<td>217,460</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>276,760</td>
<td>214,820</td>
</tr>
<tr>
<td></td>
<td>633.5</td>
<td>276,020</td>
<td>211,330</td>
</tr>
<tr>
<td>Re(_2)O(_7)(g)</td>
<td>633.5</td>
<td>258,320</td>
<td>211,330</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>258,320</td>
<td>206,470</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>258,320</td>
<td>199,060</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>258,320</td>
<td>191,660</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>258,320</td>
<td>184,250</td>
</tr>
</tbody>
</table>
Figure 4. Revised standard free energy changes for the reactions

\[
\frac{2y}{z-xy} \text{ReO}_x + O_2 = \frac{2}{z-xy} \text{Re}_y \text{O}_z,
\]
Figure 5. Phase diagram for the rhenium-oxygen system.
proposed phase diagram for the rhenium-oxygen system at one atmosphere total pressure.

There is obviously a need for more work on the rhenium-oxygen system. Heat capacity measurements on all three oxides would lead to more accurate thermodynamic functions. Identification of the gaseous species present in equilibrium with ReO$_2$ and ReO$_3$ along with determinations of their partial pressures would be in order. An accurate, consistent thermodynamic description of the rhenium-oxygen system should be possible when this work is completed.
THERMODYNAMICS OF THE MOLYBDENUM-OXYGEN SYSTEM

Introduction

Molybdenum combines with oxygen at temperatures from 300° to above 800°C to form a series of oxides, MoO₂, Mo₄₀₁₁, Mo₈₀₂₃, Mo₉₀₂₆, MoO₃. During the oxidation of molybdenum, layers of one or more of these oxides may be present on the surface of the metal. Neither the ranges of stability nor the defect structures of any of the molybdenum oxides were previously determined, making it difficult to predict the role of the various oxides in the overall oxidation process.

In this investigation the conditions of equilibrium between MoO₂ and Mo₄₀₁₁ were determined. Previous investigators determined the conditions of equilibrium between Mo and MoO₂; and when their data are combined with data from this work, the stability range of MoO₂ is fixed. It should now be possible to determine the defect structure of MoO₂ and, thus, to gain some fundamental insight into the role of MoO₂ in the oxidation of molybdenum.
Literature Survey

Properties of molybdenum

Most of the basic physical and chemical properties of molybdenum have been investigated. Recent critical evaluations of data on molybdenum such as those by Kubaschewski and Evans,39 Elliott and Gleiser,40 and Barriault et al.41 have been used to compile the list of properties in Table 9.

Table 9
Properties of Molybdenum

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>95.95</td>
<td>40</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>b.c.c.</td>
<td>39,40,41</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>( a_0 = 3.14\text{Å} )</td>
<td>39</td>
</tr>
<tr>
<td>Melting point</td>
<td>2617 ± 10°C</td>
<td>41</td>
</tr>
<tr>
<td>Boiling point</td>
<td>4692 ± 300°C</td>
<td>41</td>
</tr>
<tr>
<td>Density</td>
<td>10.3 \text{gm/cm}^3</td>
<td>40</td>
</tr>
<tr>
<td>Specific heat ((25°C))</td>
<td>5.68\text{cal/g-atom/°K}</td>
<td>40,41</td>
</tr>
</tbody>
</table>

Solubility of oxygen in molybdenum

Few and Manning42 determined that the solubility of oxygen in molybdenum varies from less than 0.03 a/o at 1100°C to almost 0.04 a/o at 1650°C.

Molybdenum oxides

Molybdenum forms a multiplicity of oxides. \(\text{MoO}_2\)
and MoO₃ are well known, and a group of oxides with compositions in the range MoO₁₂₋₂₋₇₅–MoO₃ has been studied recently. This group includes Mo₄₀¹₁, Mo₁₇₀₄₇, Mo₅₀₁₄, Mo₈₀₂₃, Mo₉₀₂₆, and Mo₁₈₀₅₂. Other oxides have been reported, notably Mo₃₀, MoO, and Mo₂O₃.

Schönberg⁴³ reported the existence of a metallic molybdenum oxide, Mo₃₀, but its existence has been disputed by Kihlborg⁴⁴ who was unsuccessful in attempts to produce it using the method described by Schönberg.⁴³ Hatterer, Herold, and Rerat⁴⁵ reacted MoO₃ with potassium vapor and treated the residue with water obtaining an insoluble, black, strongly reducing substance. X-ray analysis of the substance was interpreted as indicating the presence of Mo and an oxide, MoO. According to Kihlborg⁴⁶ the interpretation is doubtful. Watt and Davies⁴⁷ obtained an amorphous product with the composition Mo₂O₃ by reducing MoO₃ with potassium in liquid ammonia. The existences of Mo₃O, MoO, and Mo₂O₃ are certainly questionable since none of these oxides was obtained in a pure state.

The crystal structures of MoO₂, MoO₃, and the intermediate oxides have been investigated, and a summary of the data is given in Table 10. Only the latest reference, usually reporting least squares refinement of the crystal structure, is given for each oxide.

Kihlborg⁴⁶,⁵⁶ has summarized his extensive work on the crystal structures of the molybdenum oxides, and he
### Table 10
Crystal Structures of Molybdenum Oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Crystal Symmetry</th>
<th>Unit Cell Dimensions (Å, degrees)</th>
<th>Space Group</th>
<th>Cell Content</th>
<th>Reference</th>
</tr>
</thead>
</table>
| MoO₂   | Monoclinic       | **a₀ = 5.610**
  **b₀ = 4.843**
  **c₀ = 5.926**
  **β = 119.62** | P2₁ | 4MoO₂ | Magneli⁴⁸ |
| Mo₄O₁₁ | Monoclinic       | **a₀ = 24.54**
  **b₀ = 5.439**
  **c₀ = 6.701**
  **β = 94.28** | P2₁/a | 4Mo₄O₁₁ | Kihlborg⁴⁹ |
| Mo₄O₁₁ | Orthorhombic     | **a₀ = 24.49**
  **b₀ = 5.437**
  **c₀ = 6.752** | Pnma | 4Mo₄O₁₁ | Kihlborg⁴⁹ |
| Mo₁₇O₄₇ | Orthorhombic    | **a₀ = 21.61**
  **b₀ = 19.63**
  **c₀ = 3.951** | Pba₂ | 2Mo₁₇O₄₇ | Kihlborg⁵⁰ |
| Mo₅O₁₄ | Tetragonal       | **a₀ = 45.99**
  **c₀ = 5.937** | P4/n | 8Mo₅O₁₄ | Kihlborg⁵¹ |
| Mo₈O₂₃ | Monoclinic       | **a₀ = 16.88**
  **b₀ = 4.052**
  **c₀ = 13.39**
  **β = 106.19** | P2/a | 2Mo₈O₂₃ | Kihlborg⁵² |
| Mo₉O₂₆ | Monoclinic       | **a₀ = 16.74**
  **b₀ = 4.019**
  **c₀ = 14.53**
  **β = 95.45** | P2/a | 2Mo₉O₂₆ | Magneli et al.⁵³ |
| Mo₁₈O₅₂ | Triclinic       | **a₀ = 8.145**
  **b₀ = 11.89**
  **c₀ = 21.23**
  **α = 102.67**
  **β = 67.82**
  **γ = 109.97** | P | 2Mo₁₈O₅₂ | Kihlborg⁵⁴ |
| MoO₃   | Orthorhombic     | **a₀ = 3.9628**
  **b₀ = 13.855**
  **c₀ = 3.6964** | Pbnn | 4MoO₃ | Kihlborg⁵⁵ |
suggests that the oxides can be classified in four structures composed of one or more types of polyhedra. Most of the molybdenum oxides have basic structures of one of three types: rutile, ReO$_3$, and MoO$_3$. The structures of Mo$_{17}O_{47}$ and Mo$_5O_{14}$ do not have basic units, being composed of polygonal networks of polyhedra, and must be classed separately. All the oxide structures are built up of polyhedra, either Mo$_4$ tetrahedra, Mo$_6$ octahedra, or Mo$_7$ pentagonal bipyramids.

Only MoO$_2$ has a rutile structure composed of Mo$_6$ octahedra joined in strings along edges with the strings joined at octahedra corners. Magneli and Marinder$^{15}$ found short metal-metal distances within the strings of octahedra which indicates the presence of intermetallic bonding. This could explain the high electrical conductivity of MoO$_2$ found by Glemser and Lutz.$^{57}$

Both forms of Mo$_{4011}$, Mo$_{8023}$, and Mo$_9O_{26}$ all have the ReO$_3$ basic structure with the basic structure infinite in two dimensions forming finite thickness slabs. Octahedra are the only type of polyhedra involved in Mo$_{8023}$ and Mo$_9O_{26}$ with the slabs connected by octahedra sharing edges in border regions. Both octahedra and tetrahedra are involved in the two Mo$_{4011}$ structures with the slabs of octahedra connected by tetrahedra.

MoO$_3$ and Mo$_{18}O_{52}$ have the MoO$_3$ basic structure. MoO$_3$ consists of layers of zigzag strings of octahedra
sharing edges connected to adjacent strings by sharing corners. The layers are stacked so that each outside octahedral corner lies in the hole formed between four octahedra in the next layer. In Mo$_{18}^{0}O_{52}$ the layers are infinite in only one direction, forming strips of finite width. The strips are connected by a shear mechanism with some metal atoms in tetrahedral positions.

In Mo$_{17}^{0}O_{47}$ and Mo$_{5}^{0}O_{14}$ octahedra and pentagonal bipyramids are combined in complicated two-dimensional patterns involving 3, 4, 5, and 6 member rings. These networks are simply stacked together in the third dimension with the component polyhedra of each network sharing corners.

Kihlborg$^{58}$ determined the temperature range of formation of the intermediate oxides of molybdenum in the temperature range $500^\circ$ to $870^\circ$C using mixtures of MoO$_{3}$ with MoO$_{2}$ or Mo encapsulated in silica tubes. The capsules were held at constant temperatures for periods as long as several weeks and then quenched in water. The products were then analyzed by X-ray methods. Except for some minor differences, the results of Kihlborg$^{58}$ are in general agreement with those of Rode and Lysanova$^{59}$ who used both X-ray methods and differential thermal analysis. The results of both investigations are given in Table 11.

The very short heating times used by Rode and Lysanova$^{59}$ could have prevented them from observing Mo$_{17}^{0}O_{47}$ and Mo$_{5}^{0}O_{14}$ since it required several weeks for Kihlborg$^{13}$ to
Table 11
Temperature Range of Formation for Molybdenum Oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Temperature Range of Formation, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo₄O₁₁ (orthorhombic)</td>
<td>Kihlborg⁵⁸ 500 to 615 Rode and Lysanova⁵⁹ 500 to 600</td>
</tr>
<tr>
<td>Mo₄O₁₁ (monoclinic)</td>
<td>615 to 800 610 to 818-824</td>
</tr>
<tr>
<td>Mo₁₇O₄₇</td>
<td>500 to 560 Not found</td>
</tr>
<tr>
<td>Mo₅O₁₄</td>
<td>500 to 530 Not found</td>
</tr>
<tr>
<td>Mo₈O₂₃</td>
<td>650 to 780 Not found</td>
</tr>
<tr>
<td>Mo₁₈O₅₂</td>
<td>600 to 750 650 to 740</td>
</tr>
<tr>
<td>Mo₉O₂₆</td>
<td>750 to 780 750 to 779-803</td>
</tr>
</tbody>
</table>

obtain these phases. Kihlborg⁵¹ was not able to obtain a pure sample of Mo₅O₁₄ and suggests that it is metastable. Similarities of the diffraction patterns of Mo₈O₂₃ and Mo₉O₂₆ and lower resolution of the powder camera used by Rode and Lysanova⁵⁹ have been cited by Kihlborg⁴⁶ as possible reasons why Rode and Lysanova⁵⁹ did not observe Mo₈O₂₃ in their work.

The upper temperature limits given by Rode and Lysanova⁵⁹ for Mo₄O₁₁ and Mo₉O₂₆ are melting or decomposition points since the formation of a liquid phase was involved.

Eutectic reactions involving solid MoO₂ have been proposed by Galateanu⁶⁰ and Rathenau and Meijering.⁶¹ Galateanu⁶⁰ claimed a eutectic between MoO₂ and Mo₄O₁₁.
formed at 600° to 650°C, and Rathenau and Meijering\textsuperscript{61} proposed a eutectic between MoO\textsubscript{2} and MoO\textsubscript{3} at 778°C. Neither of these reactions has been confirmed, and their validity is certainly questionable.

**Thermodynamic data on molybdenum and molybdenum oxides**

The thermodynamic functions for solid molybdenum were recently compiled from the literature by Elliott and Gleiser\textsuperscript{40} and by Barriault et al.\textsuperscript{41} both giving essentially the same data for temperatures up to 1500°K. The standard entropy and heat capacity of Mo at 298.16°K are 6.83 and 5.68 cal/g-atom/°K, respectively.

MoO\textsubscript{2} and MoO\textsubscript{3} have been extensively investigated, especially using calorimetric methods. King, Weller, and Christensen\textsuperscript{36} present a complete, consistent compilation of the calorimetric data on MoO\textsubscript{2} and MoO\textsubscript{3} based on investigations carried out at the Berkeley Bureau of Mines Thermodynamics Laboratory. These investigations include determinations of the heat of formation of MoO\textsubscript{2} and MoO\textsubscript{3} by Mah,\textsuperscript{62} of the low temperature heat capacity of MoO\textsubscript{2} by King,\textsuperscript{63} and of MoO\textsubscript{3} by Kelley and King,\textsuperscript{64} and of the high temperature heat capacities and entropies of MoO\textsubscript{2} and MoO\textsubscript{3} by King, Weller, and Christensen.\textsuperscript{36} A partial list of the thermodynamic functions recommended by King, Weller, and Christensen\textsuperscript{36} is given in Table 12.
Table 12
Thermodynamic Functions for MoO$_2$ and MoO$_3$

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Function</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_2$(c)</td>
<td>$\Delta H_f^{\circ}$,298.16</td>
<td>-140.8±0.2</td>
<td>Kcal/mole</td>
<td>Mah$^{62}$</td>
</tr>
<tr>
<td></td>
<td>$S^{\circ}$,298.16</td>
<td>11.06±0.05</td>
<td>cal/mole/°K</td>
<td>King$^{63}$</td>
</tr>
<tr>
<td></td>
<td>$C^{p,\circ}$,298.16</td>
<td>13.38</td>
<td>cal/mole/°K</td>
<td>King$^{63}$</td>
</tr>
<tr>
<td>MoO$_3$(c)</td>
<td>$\Delta H_f^{\circ}$,298.16</td>
<td>-178.1±0.1</td>
<td>Kcal/mole</td>
<td>Mah$^{62}$</td>
</tr>
<tr>
<td></td>
<td>$S^{\circ}$,298.16</td>
<td>18.58±0.10</td>
<td>cal/mole/°K</td>
<td>Kelley and King$^{64}$</td>
</tr>
<tr>
<td></td>
<td>$C^{p,\circ}$,298.16</td>
<td>17.92</td>
<td>cal/mole/°K</td>
<td>Kelley and King$^{64}$</td>
</tr>
</tbody>
</table>

The melting point, heat of fusion, and heat capacity of liquid MoO$_3$ given by King, Weller, and Christensen$^{36}$ are 1074°K, 11,690 cal/mole, and 30.20 cal/mole/°K, respectively. The melting point of MoO$_3$ was determined to be 1068°K by Hoermann$^{65}$ and by Cosgrove and Snyder$^{66}$ and to be 1070°K by Babadzhan.$^{67}$ A value of 1070° ±5°K is recommended by Barriault et al.$^{41}$ A heat of fusion of 12,540 cal/mole was determined by Cosgrove and Snyder,$^{66}$ assuming a constant heat capacity of liquid MoO$_3$ equal to 32.0 cal/mole/°K. A heat of fusion almost identical to that given by King, Weller, and Christensen$^{36}$ is recommended by Barriault et al.$^{41}$ along with the heat capacity of liquid MoO$_3$ equal to 30.20 cal/mole/°K. With the exception of the melting point of MoO$_3$,
the data on MoO₂ and MoO₃ given in the compilation of Barriault et al.⁴¹ are essentially the same as those of King, Weller, and Christensen.³⁶

According to King, Weller, and Christensen³⁶ MoO₂ does not melt but instead disproportionates to yield one atmosphere pressure of gaseous MoO₃ at 2600°K.

The high temperature equilibrium between Mo and MoO₂ has been recently investigated using gas techniques by Gleiser and Chipman⁶⁸ and using solid electrolyte galvanic cells by Rapp³³ and by Barbi.⁶⁹ From these investigations the following equations for the standard molar free energy change for formation for MoO₂ were derived:

\[ \Delta F^0_T = -137890 + 40.18T, \text{ cal/mole (Gleiser and Chipman}^{68}) \]  \hspace{1cm} (43)

\[ \Delta F^0_T = -137500 + 40.00T, \text{ cal/mole (Rapp}^{33}), \]  \hspace{1cm} (44)

and

\[ \Delta F^0_T = -138350 + 42.5T, \text{ cal/mole (Barbi}^{69}) \]  \hspace{1cm} (45)

The temperature interval from 926° to 1068°C was investigated by Gleiser and Chipman,⁶⁸ and the slope in their equation is derived from calorimetric work. Rapp³³ covered the temperature interval from 750° to 1050°C, and the slope in his equation was derived from the experimental data. The results obtained by Barbi⁶⁹ give \( \Delta F^0_T \) values considerably lower than those of Gleiser and Chipman⁶⁸ and Rapp³³. Barbi⁶⁹ admits that his results were hardly reproducible, with penetration of the electrolyte and attack of the
reference electrode by volatile MoO$_3$ both occurring. Rapp$^{33}$ used a technique similar to that of Barbi;$^{69}$ but in his work special precautions were taken to prevent side reactions with the atmosphere, and two different reference electrodes were used to provide independent determinations.

The results of Gleiser and Chipman$^{68}$ and Rapp$^{33}$ are in very good agreement. Their results give $\Delta F^o_T$ values several hundred calories more negative at high temperatures than those of King, Weller, and Christensen.$^{36}$ Since it is based on equilibrium measurements over an extended range at high temperatures, the equation for $\Delta F^o_T$ derived by Rapp$^{33}$ is preferred.

Two investigations of the reduction of MoO$_3$ by hydrogen and hydrogen-water vapor mixtures have been reported. Thermogravimetric curves for the reduction of MoO$_3$, MoO$_2$.89, MoO$_2$.75, and MoO$_2$ were obtained by Hegedus, Sasvari, and Neugebauer.$^{70}$ Sardi$^{71}$ used hydrogen-water vapor mixtures with the ratio $P_{H_2O}/P_{H_2}$ varied from 0.02 to 10,000 to study the reduction of MoO$_3$. In both investigations X-ray analysis was used to identify the end products. Neither of these investigations could be used to derive thermodynamic data. Sardi$^{71}$ points out that his results cannot be interpreted to give a phase equilibrium diagram, but instead, an "appearance of kinetical phases" diagram.

Some thermodynamic functions for the intermediate oxides have been estimated by Brewer$^{23}$ and by Kubaschewski
Table 13
Thermodynamic Functions for the Intermediate Molybdenum Oxides Estimated by Brewer\textsuperscript{23}

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$\Delta F_{298}$ (Kcal/mole)</th>
<th>$\Delta H_{298}$ (Kcal/mole)</th>
<th>$\Delta S_{298}$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{11} \text{ Mo}<em>4\text{O}</em>{11}$</td>
<td>-56</td>
<td>-61 ± 2</td>
<td>-20</td>
</tr>
<tr>
<td>$\frac{1}{23} \text{ Mo}<em>8\text{O}</em>{23}$</td>
<td>-54.5</td>
<td>-60.5 ± 2</td>
<td>-20</td>
</tr>
<tr>
<td>$\frac{1}{26} \text{ Mo}<em>9\text{O}</em>{26}$</td>
<td>-54.5</td>
<td>-60.5 ± 2</td>
<td>-20</td>
</tr>
</tbody>
</table>

and Evans.\textsuperscript{72} Kubaschewski and Evans\textsuperscript{72} estimated the heat of formation of $\text{Mo}_4\text{O}_{11}$ at 298°C to be $-674 ±$ Kcal/mole. The estimates by Brewer\textsuperscript{23} are listed above in Table 13. Brewer\textsuperscript{23} suggests that $\text{Mo}_4\text{O}_{11}$, $\text{Mo}_8\text{O}_{23}$, and $\text{Mo}_9\text{O}_{26}$ all disproportionate at high temperatures.

Blackburn, Hoch, and Johnston\textsuperscript{73} measured the vapor pressure of gaseous $\text{Mo}_3$ over mixtures of $\text{MoO}_2$ and $\text{Mo}_4\text{O}_{11}$ at 607°C and used their data to estimate a heat of formation of $\text{Mo}_4\text{O}_{11}$ equal to $-664 ± 6.4$ Kcal/mole.

Berkowitz, Inghram, and Chupka\textsuperscript{74} used the mass spectrometer method to determine the vapor species over $\text{Mo}_3$. The trimer, $(\text{Mo}_3)_3$, was the main species found along with $\text{Mo}_3$, $(\text{Mo}_3)_2$, $(\text{Mo}_3)_4$, and $(\text{Mo}_3)_5$ in smaller quantities. Gulbransen, Andrew, and Brassart\textsuperscript{75} recently reviewed the vapor pressure data for solid and liquid $\text{Mo}_3$ and proposed these equations.
Experimental Procedure

Two series of experiments were carried out in this investigation of the thermodynamics of the molybdenum-oxygen system. In one series solid electrolyte, galvanic cells were used to determine the free energy of formation of Mo\(_{4}\)O\(_{11}\). The other series of experiments consisted of equilibrations of molybdenum oxides using various oxygen-molybdenum ratios over a range of temperatures. The latter series was used to determine the peritectic temperature for the reaction between MoO\(_{2}\), Mo\(_{4}\)O\(_{11}\), and MoO\(_{3}\).

Free energy of formation of Mo\(_{4}\)O\(_{11}\)

The free energy of formation of Mo\(_{4}\)O\(_{11}\) was determined using the same technique and equipment as that used...
to determine the free energy of formation of ReO$_2$. The only differences were that the electrodes were MoO$_2$-Mo$_4$O$_{11}$ and either Fe-Fe$_x$O or Ni-NiO. The cells are schematically shown as

$$\text{Pt} | \text{Ni,NiO} | \text{Zr}_{0.85}\text{Ca}_{0.15}O_{1.85} | \text{MoO}_2,\text{Mo}_4\text{O}_{11} | \text{Pt},$$

and

$$\text{Pt} | \text{Fe,Fe}_x\text{O} | \text{Zr}_{0.85}\text{Ca}_{0.15}O_{1.85} | \text{MoO}_2,\text{Mo}_4\text{O}_{11} | \text{Pt}.$$ 

The cell reactions were

$$\text{Mo}_4\text{O}_{11}(c) + 3\text{Ni}(c) = 4\text{MoO}_2(c) + 3\text{NiO}(c),$$

and

$$\text{Mo}_4\text{O}_{11}(c) + 3\text{xFe}(c) = 4\text{MoO}_2(c) + 3\text{Fe}_x\text{O}(c).$$

The Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ electrolyte crucibles were made by using the same technique as that described in the section on ReO$_2$. The MoO$_2$-Mo$_4$O$_{11}$ powder mixture for the electrode was made by reacting MoO$_2$ and MoO$_3$ in an atom ratio 0/Mo = 2.25 at 810°C for 48 hours in a sealed, evacuated vycor capsule. The MoO$_2$ and MoO$_3$ had been previously made by oxidizing Mo powder in CO-CO$_2$ or O$_2$-argon gas mixtures. The Ni-NiO electrodes were the same as those used in the ReO$_2$ work. The Fe-Fe$_x$O electrode was made from zone-refined iron. A solid piece of iron was cut up using a milling machine. The milled pieces were then oxidized in CO-CO$_2$ mixtures at about 900°C to make Fe$_x$O. The resulting pieces
of oxide were then ground in a mortar and pestle. Part of the FeO powder was then reduced to Fe by using reducing CO-CO$_2$ mixtures. Chemical analyses of the starting materials are reported in Table 3. The phases present in each electrode were checked before and after each experiment using X-ray diffraction, as in the ReO$_2$ work.

In this work the temperature range covered was from about 650°C to 830°C. The lower limit was again fixed by the electrolyte while the upper limit was fixed by the decomposition of Mo$_4$O$_{11}$ to MoO$_2$ plus liquid MoO$_3$. The latter coated the Pt lead and apparently caused a blocking condition to develop. The emf quickly decayed to zero every time the temperature of a cell exceeded about 825°C, and after this point was reached the cell could not be used any longer even at lower temperatures.

**Peritectic decomposition of Mo$_4$O$_{11}$**

The temperature for the peritectic reaction

$$\text{Mo}_4\text{O}_{11} (c) = \text{MoO}_2 (c) + 3\text{MoO}_3 (l)$$

was determined by encapsulating mixtures of MoO$_2$ and MoO$_3$ in various ratios, equilibrating them at temperatures from 800°C to 840°C, quenching the capsules, and then analyzing the product by X-ray diffraction techniques.

The starting materials, MoO$_2$ and MoO$_3$, were the same as those described previously. These were mixed to
give atom ratios 0/Mo of 2.25, 2.5, 2.6, 2.7, 2.75, 2.8, and 2.85. The mixtures were sealed into evacuated vycor capsules. The capsules were heat treated at a constant temperature for periods of 12 to 16 hours and then quenched into water. Each capsule was then broken open, and the contents were removed and then ground in a mortar and pestle. A sample of the resulting powder was then used for X-ray diffraction analysis, and the remainder of the powder was sealed into another capsule. This was repeated for all of the capsules. The group of new capsules filled with previously heat treated materials was then heat treated again at the same temperature. The whole process was repeated until only two phases were present, and the same two phases were present after at least two cycles of heat treatment. The equilibrations were carried out at several temperatures between 800° and 840°C with most of them in the range from 815° to 830°C.

The appearance of the sample was noted after each heat treating cycle, and it was easily determined whether the mixture had either sintered or melted. Some fogging of the vycor was noted at the higher ratios and at higher temperatures. No evidence of gross attack on the vycor by the liquid MoO₃ was observed.
Results

Free energy of formation of Mo$_4$O$_{11}$

Two separate runs were made with each of the cells,

I. Pt $|$ Ni,NiO $|$ Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ $|$ MoO$_2$,Mo$_4$O$_{11}$ $|$ Pt

and

II. Pt $|$ Fe,Fe$_x$O $|$ Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$ $|$ MoO$_2$,Mo$_4$O$_{11}$ $|$ Pt.

Eight to ten values of the reversible emf at different temperatures were obtained on each run. The time required to reach reversible conditions varied from several hours to about one day with the longer times needed at low temperatures. The emf data were interpreted according to the reactions,

$$\frac{2}{3}\text{Mo}_4\text{O}_{11}(c) + 2\text{Ni}(c) = \frac{8}{3}\text{MoO}_2(c) + 2\text{NiO}(c),$$

and

$$\frac{2}{3}\text{Mo}_4\text{O}_{11}(c) + 2\text{Fe}(c) = \frac{8}{3}\text{MoO}_2(c) + 2\text{Fe}_x\text{O}(c).$$

The cell emf, the free energy change for the cell reaction, and the partial molar free energy of oxygen for each electrode are related for the cells according to

$$\Delta F_{\text{cell } I} = -4\mathcal{E}_I = F_{O_2}(\text{Ni,NiO}) - F_{O_2}(\text{MoO}_2,\text{Mo}_4\text{O}_{11}), \quad (48)$$

and

$$\Delta F_{\text{cell } II} = -4\mathcal{E}_{II} = F_{O_2}(\text{Fe,Fe}_x\text{O}) - F_{O_2}(\text{MoO}_2,\text{Mo}_4\text{O}_{11}). \quad (49)$$
By using the arguments developed previously in the section on $\Delta F^o_{\text{ReO}_2}$ and substituting the standard molar free energies of formation of NiO and Fe$\text{O}_x$, equations (48) and (49) may be rearranged, obtaining

$$\Delta F^o_{(\text{MoO}_2, \text{Mo}_4\text{O}_{11})} = 4\epsilon I + 2\Delta F^o_{\text{NiO}}, \quad (50)$$

and

$$\Delta F^o_{(\text{MoO}_2, \text{Mo}_4\text{O}_{11})} = 4\epsilon II + 2\Delta F^o_{\text{Fe}_x\text{O}}. \quad (51)$$

$\Delta F^o_{(\text{MoO}_2, \text{Mo}_4\text{O}_{11})}$ is the standard free energy change for the reaction

$$\frac{8}{3}\text{MoO}_2(c) + \text{O}_2(g) = \frac{2}{3}\text{Mo}_4\text{O}_{11}(c).$$

The following equations, based on the investigations recommended by Chipman, were used to calculate $\Delta F^o_{\text{NiO}}$ and $\Delta F^o_{\text{Fe}_x\text{O}}$.

$$\Delta F^o_{\text{NiO}} = -56000 + 20.3T \text{ cal/mole}, \quad (52)$$

and

$$\Delta F^o_{\text{Fe}_x\text{O}} = -63200 + 15.6T \text{ cal/mole}. \quad (53)$$

When equations (52) and (53) are substituted into equations (50) and (51), the equations used to evaluate the data are obtained

$$\Delta F^o_{(\text{MoO}_2, \text{Mo}_4\text{O}_{11})} = -112000 + 40.6T + 92252 \epsilon I, \quad (54)$$

and

$$\Delta F^o_{(\text{MoO}_2, \text{Mo}_4\text{O}_{11})} = -126400 + 31.2T + 92252 \epsilon II. \quad (55)$$
The experimental values of the temperature and emf and the values of $\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})}$ are given in Table 14.

The standard deviations in the reversible emf values were less than 0.0005 volt at each temperature, and this contributes an error of $\pm 50$ cal to the calculated $\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})}$ values. When the error from the deviations of the emf values is added to the error in the reference electrode equations, $\pm 100$ cal, a probable error for the $\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})}$ values in Table 14 of $\pm 150$ cal results.

The data for each reference electrode were analyzed by the least squares method. The following equations were obtained:

$$\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})} = -86430 + 42.37T, \text{ for Ni-NiO,} \quad (56)$$

and

$$\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})} = -86220 + 42.03T, \text{ for Fe}_x\text{O}. \quad (57)$$

These equations give values of $\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})}$ that agree within less than 200 cal for temperatures in the vicinity of $1000^\circ\text{K}$. An average of equations (56) and (57) is recommended for $\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})}$

$$\Delta F^\circ_{(\text{MoO}_2,\text{Mo}_4\text{O}_{11})} = -86330 + 42.2T \pm 300, \text{ cal/mole} \quad (58)$$

The probable error of $\pm 300$ cal is estimated by using the error values of $\pm 100$ cal recommended for equations (52)
Table 14
Free Energy of Formation of Mo$_4$O$_{11}$ Data

<table>
<thead>
<tr>
<th>Reference Electrode</th>
<th>Temperature ($^\circ$K)</th>
<th>emf (volts)</th>
<th>$\Delta F^\circ$ (MoO$_2$, Mo$<em>4$O$</em>{11}$) (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-NiO</td>
<td>919.1</td>
<td>0.2946</td>
<td>47,510</td>
</tr>
<tr>
<td></td>
<td>922.2</td>
<td>0.2952</td>
<td>47,330</td>
</tr>
<tr>
<td></td>
<td>939.3</td>
<td>0.2952</td>
<td>46,630</td>
</tr>
<tr>
<td></td>
<td>942.0</td>
<td>0.2952</td>
<td>46,320</td>
</tr>
<tr>
<td></td>
<td>957.3</td>
<td>0.2962</td>
<td>45,810</td>
</tr>
<tr>
<td></td>
<td>961.3</td>
<td>0.2950</td>
<td>45,760</td>
</tr>
<tr>
<td></td>
<td>979.2</td>
<td>0.2961</td>
<td>44,930</td>
</tr>
<tr>
<td></td>
<td>980.8</td>
<td>0.2964</td>
<td>44,840</td>
</tr>
<tr>
<td></td>
<td>998.9</td>
<td>0.2957</td>
<td>44,170</td>
</tr>
<tr>
<td></td>
<td>1001.0</td>
<td>0.2965</td>
<td>44,010</td>
</tr>
<tr>
<td></td>
<td>1018.8</td>
<td>0.2964</td>
<td>43,290</td>
</tr>
<tr>
<td></td>
<td>1021.5</td>
<td>0.2966</td>
<td>43,160</td>
</tr>
<tr>
<td></td>
<td>1040.1</td>
<td>0.2978</td>
<td>42,300</td>
</tr>
<tr>
<td></td>
<td>1042.2</td>
<td>0.2967</td>
<td>42,310</td>
</tr>
<tr>
<td></td>
<td>1059.7</td>
<td>0.3001</td>
<td>41,490</td>
</tr>
<tr>
<td></td>
<td>1063.6</td>
<td>0.2972</td>
<td>41,400</td>
</tr>
<tr>
<td></td>
<td>1077.5</td>
<td>0.2977</td>
<td>40,790</td>
</tr>
<tr>
<td></td>
<td>1080.8</td>
<td>0.2981</td>
<td>40,620</td>
</tr>
<tr>
<td>Fe-Fe$_x$O</td>
<td>919.4</td>
<td>0.5438</td>
<td>47,550</td>
</tr>
<tr>
<td></td>
<td>926.2</td>
<td>0.5444</td>
<td>47,280</td>
</tr>
<tr>
<td></td>
<td>924.0</td>
<td>0.5437</td>
<td>47,410</td>
</tr>
<tr>
<td></td>
<td>948.6</td>
<td>0.5479</td>
<td>46,255</td>
</tr>
<tr>
<td></td>
<td>951.5</td>
<td>0.5474</td>
<td>46,215</td>
</tr>
<tr>
<td></td>
<td>959.7</td>
<td>0.5475</td>
<td>45,950</td>
</tr>
<tr>
<td></td>
<td>966.4</td>
<td>0.5477</td>
<td>45,725</td>
</tr>
<tr>
<td></td>
<td>977.3</td>
<td>0.5502</td>
<td>45,150</td>
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<tr>
<td></td>
<td>981.8</td>
<td>0.5504</td>
<td>44,990</td>
</tr>
<tr>
<td></td>
<td>1001.1</td>
<td>0.5535</td>
<td>44,100</td>
</tr>
<tr>
<td></td>
<td>1002.3</td>
<td>0.5528</td>
<td>44,130</td>
</tr>
<tr>
<td></td>
<td>1023.0</td>
<td>0.5560</td>
<td>43,190</td>
</tr>
<tr>
<td></td>
<td>1025.7</td>
<td>0.5557</td>
<td>43,140</td>
</tr>
<tr>
<td></td>
<td>1046.5</td>
<td>0.5587</td>
<td>42,210</td>
</tr>
<tr>
<td></td>
<td>1050.1</td>
<td>0.5581</td>
<td>42,150</td>
</tr>
<tr>
<td></td>
<td>1069.9</td>
<td>0.5618</td>
<td>41,190</td>
</tr>
<tr>
<td></td>
<td>1071.9</td>
<td>0.5610</td>
<td>41,200</td>
</tr>
<tr>
<td></td>
<td>1080.5</td>
<td>0.5624</td>
<td>40,810</td>
</tr>
<tr>
<td></td>
<td>1083.9</td>
<td>0.5625</td>
<td>50,690</td>
</tr>
<tr>
<td></td>
<td>1087.8</td>
<td>0.5633</td>
<td>40,490</td>
</tr>
</tbody>
</table>
and (53) and the good agreement of equations (56) and (57). The data points calculated from equations (54) and (55) are shown in Figure 6 along with plots of the least squares equations (56) and (57).

The quantity \( \Delta F^\circ(\text{Mo}_0^2, \text{Mo}_4^0 11) \) is related to the standard molar free energies of formation of MoO\(_2\) and Mo\(_4^0 11\) by

\[
\Delta F^\circ(\text{Mo}_0^2, \text{Mo}_4^0 11) = \frac{2}{3} \Delta F^\circ \text{Mo}_4^0 11 = \frac{5}{3} \Delta F^\circ \text{Mo}_0^2 . \tag{59}
\]

The equation for the standard molar free energy of Mo\(_4^0 11\) is then obtained:

\[
\Delta F^\circ \text{Mo}_4^0 11 = \frac{2}{3} \Delta F^\circ(\text{Mo}_0^2, \text{Mo}_4^0 11) + 4 \Delta F^\circ \text{Mo}_0^2 . \tag{60}
\]

Substituting equation (58) for \( \Delta F^\circ(\text{Mo}_0^2, \text{Mo}_4^0 11) \) and the equation given by Rapp\(^3\) for \( \Delta F^\circ \text{Mo}_0^2 \),

\[
\Delta F^\circ \text{Mo}_0^2 = -137500 + 40.0T, \text{ cal/mole}, \tag{61}
\]

into equation (60), the following equation for \( \Delta F^\circ \text{Mo}_4^0 11 \) is obtained:

\[
\Delta F^\circ \text{Mo}_4^0 11 = -679500 + 223.3T, \text{ cal/mole} . \tag{62}
\]

The range of error for equation (62) would be \( \pm 1250 \) cal assuming a probable error of \( \pm 200 \) cal for equation (61) and adding this to the estimated error in \( \Delta F^\circ(\text{Mo}_0^2, \text{Mo}_4^0 11) \).
Figure 6. Experimental $\Delta F^\circ_{(MoO_2,Mo_4O_{11})}$ values versus temperature.
It is important to note the choices of standard states in the preceding analysis. The standard state for oxygen gas is that state in which the fugacity is equal to one for the temperature under consideration. The standard states for the metals, Ni, Fe, and Mo are the metals saturated with their respective oxides at one atmosphere pressure and the temperature under consideration. Similarly, the standard states for Ni and Fe are the oxides saturated with the metals at one atmosphere pressure and the temperature under consideration. The choice of the standard state for MoO$_2$ is more difficult since it is considered to be in equilibrium with Mo in one instance and Mo$_4$O$_{11}$ in another. For equilibrium with Mo the standard state of MoO$_2$ is MoO$_2$ saturated with Mo at one atmosphere total pressure and the temperature under consideration, and for equilibrium with Mo$_4$O$_{11}$ the standard state is MoO$_2$ saturated with Mo$_4$O$_{11}$ at one atmosphere pressure and the temperature under consideration. In deriving equation (62) both of the standard states of MoO$_2$ are involved, and they are assumed to be equivalent. This assumption is legitimate if the homogeneity range of MoO$_2$ is small. The lack of data on the homogeneity range of MoO$_2$ prevents checking the validity of this assumption. Finally, the standard state of Mo$_4$O$_{11}$ is Mo$_4$O$_{11}$ saturated with MoO$_2$ at one atmosphere pressure and the temperature under consideration.
In formulating the reactions in this section and the one which follows, it is assumed that MoO\textsubscript{2}, Mo\textsubscript{4}O\textsubscript{11}, and MoO\textsubscript{3} are stoichiometric in composition.

**Peritectic decomposition of Mo\textsubscript{4}O\textsubscript{11}**

The presence of a liquid phase in a capsule at the equilibration temperature could be inferred from the appearance of the material after quenching. For compositions MoO\textsubscript{2.8} and MoO\textsubscript{2.85} a liquid phase was present at all temperatures above 800°C. For compositions MoO\textsubscript{2.75} and lower a liquid phase was present above 825°C. Below 825°C Mo\textsubscript{4}O\textsubscript{11} was present in every case with MoO\textsubscript{2} present for compositions less than MoO\textsubscript{2.75} and MoO\textsubscript{3} present for compositions greater than MoO\textsubscript{2.75}. Only MoO\textsubscript{2} and MoO\textsubscript{3} were present above 825°C. The liquid phase is assumed to have a composition near or equal to MoO\textsubscript{3}. From this information it is concluded that Mo\textsubscript{4}O\textsubscript{11} decomposes according to the peritectic reaction

\[
\text{Mo}_4\text{O}_{11}(c) = \text{MoO}_2(c) + 3\text{MoO}_3(l)
\]

at 825°C.

**Discussion**

The standard molar free energy of formation of Mo\textsubscript{4}O\textsubscript{11} given by equation (62) is the first thermodynamic function to be experimentally determined for any of the intermediate oxides of molybdenum. The validity of this function cannot
be directly examined, but it can be assessed in terms of how well it combines with the functions for MoO₂ and MoO₃ to predict known reactions in the molybdenum-oxygen system.

The occurrence of the peritectic reaction between Mo₄O₁₁, MoO₂, and MoO₃ dictates that the free energy changes for the reactions

\[
\frac{8}{3} \text{MoO}_2(c) + \text{O}_2(g) = \frac{2}{3} \text{Mo}_4\text{O}_{11}(c),
\]

and

\[
2\text{MoO}_2(c) + \text{O}_2(g) = 2\text{MoO}_3(1)
\]

are equal at 825°C. Using equation (61) for \( \Delta F^\circ_{\text{MoO}_2} \), equation (62) for \( \Delta F^\circ_{\text{Mo}_4\text{O}_{11}} \), and \( \Delta F^\circ_{\text{MoO}_3} \) values from Barriault et al., the standard free energy change is -39990 cal for the first reaction and -38530 cal for the second reaction. This is satisfactory agreement considering that the \( \Delta F^\circ_{\text{MoO}_3} \) values are based on calorimetric data while the \( \Delta F^\circ_{\text{MoO}_2} \) and \( \Delta F^\circ_{\text{Mo}_4\text{O}_{11}} \) values are based on equilibrium experiments.

The \( \Delta F^\circ \) values shown in Figure 7 for the MoO₂(c)-MoO₃(1) and Mo₄O₁₁(c)-MoO₃(c,1) equilibria have been adjusted to fit with MoO₂(c)-Mo₄O₁₁(c) equilibrium by making the \( \Delta F^\circ_{\text{MoO}_3} \) values more negative by 730 cal/mole. An extended range of homogeneity for liquid MoO₃ could account for this difference since the calorimetric value is associated with stoichiometric MoO₃. Liquid MoO₃ in equilibrium
Figure 7. Standard free energy changes for the reactions.

\[
\frac{2y}{wz-xy} \text{Mo}_x\text{O}_y + \text{O}_2 = \frac{2wy}{wz-xy} \text{Mo}_y\text{O}_2.
\]
with either MoO$_2$ or Mo$_4$O$_{11}$ could be considerably oxygen deficient. Similarly, the differences between the $\Delta F^\circ_{\text{MoO}_2}$ values of Rapp$^{33}$ and those of King, Weller, and Christensen$^{36}$ could be due to oxygen deficiency of MoO$_2$ in equilibrium with Mo. In each case the difference is associated with the integral, $\int \Delta F_{\text{O}_2} \ d(N_0/N_{\text{Mo}})$, taken over the range of homogeneity. The lack of information on the homogeneity ranges of MoO$_2$ and MoO$_3$ prevents an evaluation of these differences.

Due to a lack of data, the diagram cannot be accurately constructed in the regions of free energies and temperatures corresponding to the various equilibria among Mo$_4$O$_{11}$, the other intermediate oxides, and MoO$_3$. Mo$_8$O$_{23}$ and Mo$_9$O$_{26}$ both decompose at about 780°C according to Kihlborg,$^{58}$ and the Mo$_4$O$_{11}$(c)-MoO$_3$(c,1) equilibrium represented in Figure 7 down to 780°C is believed to be accurate based on the assumption that the melting point of MoO$_3$ is independent of the oxygen pressure. Estimated values for the equilibria involving Mo$_8$O$_{23}$, Mo$_9$O$_{26}$, and Mo$_{17}$O$_{47}$ were used in constructing Figure 7. These estimated values are entirely speculative and may be considerably in error.

A temperature versus composition diagram derived from Figure 7 is shown in Figure 8. In constructing Figures 7 and 8 the solid-state phase transformations in Mo$_4$O$_{11}$ and Mo$_9$O$_{26}$ were ignored, and these phases are designated only by their chemical formulas. Mo$_8$O$_{23}$ and Mo$_9$O$_{26}$ are
Figure 8. Phase diagram for the molybdenum-oxygen system.
assumed to be stable at all temperatures below 780°C although Kihlborg suggests that these phases may be unstable at low temperatures. The decomposition temperature of Mo$_{8}O_{23}$ was assumed to be slightly higher than that of Mo$_{9}O_{26}$ in constructing Figures 7 and 8. If the decomposition order were reversed, only slight changes in each diagram would result.

The standard enthalpy and entropy of formation of Mo$_{4}O_{11}$ can be derived from the equation for the standard free energy of formation,

$$\Delta F^\circ_{Mo_4O_{11}} = -679500 + 223.3T \text{ cal/mole}.$$  \hspace{1cm} (62)

The average temperature for the data taken in this investigation is almost equal to 1000°K, and using the equations

$$\Delta S^\circ = -\left(\frac{d\Delta F^\circ}{dT}\right)_p,$$  \hspace{1cm} (63)

and

$$\Delta H^\circ = \frac{d(AF^\circ/T)}{d(1/T)}_p,$$  \hspace{1cm} (64)

the standard enthalpy and entropy of formation of Mo$_{4}O_{11}$ at 1000°K can be derived. The values of these functions are

$$\Delta H^\circ_{Mo_4O_{11}} = -679500, \text{ cal/mole},$$  \hspace{1cm} (65)

and

$$\Delta S^\circ_{Mo_4O_{11}} = -223.3, \text{ cal/mole/°K},$$  \hspace{1cm} (66)

at 1000°K.
Extrapolation of the thermodynamic functions to temperatures outside the range of direct observation requires information on the heat capacities of the reacting substances. In the absence of heat capacity data for Mo$_4$O$_{11}$ or any similar compound, there is no choice but to estimate the change of heat capacity for the reaction

$$4\text{Mo}(c) + \frac{11}{2}\text{O}_2(g) = \text{Mo}_4\text{O}_{11}(c).$$

Using the average values recommended by Kubaschewski and Evans, the change of heat capacity is estimated to be 16.5 cal/mole/°K. The estimated $\Delta C_p$ value may be combined with the standard enthalpy and entropy of formation at 1000°K to estimate the enthalpy and entropy at any temperature using the equations

$$\Delta H_T^0 = \Delta H_{1000}^0 - \int_{T}^{1000} \frac{T}{\Delta C_p} \,dT , \quad (67)$$

and

$$\Delta S_T^0 = \Delta S_{1000}^0 - \int_{T}^{1000} \frac{T}{\Delta C_p} \,dT . \quad (68)$$

Substituting 16.5 cal/mole/°K for $\Delta C_p$ and integrating equations (67) and (68) yields

$$\Delta H_T^0 = -696000 + 16.5% \text{ cal/mole} , \quad (69)$$

and

$$\Delta S_T^0 = -337.3 + 38.0 \log T \text{ cal/mole/°K} . \quad (70)$$

Similarly, the standard free energy of formation is given by the equation
\[ \Delta F^\circ_T = -696000 - 38.0T \log T + 353.8T \text{cal/mole}. \quad (71) \]

Finally, the standard entropy of Mo\(_4\)\(\text{O}_{11}\) may be calculated by using the equation

\[ S^\circ_{\text{Mo}_4\text{O}_{11}} = \Delta S^\circ + 4S^\circ_{\text{Mo}} + 5.5S^\circ_{\text{O}_2}. \quad (72) \]

Values of the thermodynamic functions for Mo\(_4\)\(\text{O}_{11}\), \(S^\circ_{\text{Mo}_4\text{O}_{11}}\), \(\Delta S^\circ_f\), \(\Delta H^\circ_f\), and \(\Delta F^\circ_f\) are given in Table 15 for temperatures from 298° to 1098°K in 100° intervals. The \(S^\circ_{\text{Mo}_4\text{O}_{11}}\) values were calculated by using equation (72) with values of \(S^\circ_{\text{O}_2}\) and \(S^\circ_{\text{Mo}}\) taken from Wicks and Block\(^7\) and Barriault et al.\(^4\) respectively. The \(\Delta H^\circ_f\), \(\Delta S^\circ_f\), and \(\Delta F^\circ_f\) values were calculated by using equations (69), (70), and (71), respectively.
Table 15
Thermodynamic Functions for Mo$_4$O$_{11}$(c)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$S^0$ (cal/mole/°K)</th>
<th>$-\Delta S_f^0$ (cal/mole/°K)</th>
<th>$-\Delta H_f^0$ (cal/mole)</th>
<th>$-\Delta F_f^0$ (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>53.6</td>
<td>243.3</td>
<td>691,100</td>
<td>618,600</td>
</tr>
<tr>
<td>400</td>
<td>77.0</td>
<td>238.4</td>
<td>689,400</td>
<td>594,050</td>
</tr>
<tr>
<td>500</td>
<td>95.0</td>
<td>234.7</td>
<td>687,750</td>
<td>570,400</td>
</tr>
<tr>
<td>600</td>
<td>110.1</td>
<td>231.7</td>
<td>686,100</td>
<td>547,100</td>
</tr>
<tr>
<td>700</td>
<td>123.1</td>
<td>229.2</td>
<td>684,450</td>
<td>524,000</td>
</tr>
<tr>
<td>800</td>
<td>134.6</td>
<td>227.0</td>
<td>682,800</td>
<td>501,200</td>
</tr>
<tr>
<td>900</td>
<td>145.0</td>
<td>225.0</td>
<td>681,150</td>
<td>478,600</td>
</tr>
<tr>
<td>1000</td>
<td>154.4</td>
<td>223.3</td>
<td>679,500</td>
<td>456,200</td>
</tr>
<tr>
<td>1098</td>
<td>162.9</td>
<td>221.8</td>
<td>677,900</td>
<td>434,500</td>
</tr>
</tbody>
</table>
DEFECT STRUCTURE OF ALPHA TANTALUM PENTOXIDE

Introduction

Tantalum is unique among the refractory metals in forming only a single thermodynamically stable oxide, Ta$_2$O$_5$, in the condensed states. Various suboxides have been reported for tantalum, but all of these are believed to be metastable oxidation products formed at low temperatures. Ta$_2$O$_5$ is a relatively stable oxide having a slightly greater stability than Cr$_2$O$_3$. The melting point of Ta$_2$O$_5$ is 1873°C which is among the highest of the oxides of the refractory metals. The phase transformation from β-Ta$_2$O$_5$ to α-Ta$_2$O$_5$ occurs at 1360°C on heating and is not destructive in the usual sense. α-Ta$_2$O$_5$ can easily be retained at room temperature on cooling from above 1360°C, and with care it can be shaped by ordinary methods. Ta$_2$O$_5$ is an electrical insulator at low temperatures with its conductivity increasing to the semiconductor range at temperatures above about 1200°C. These properties almost place Ta$_2$O$_5$ in the refractory oxide class with Cr$_2$O$_3$, Al$_2$O$_3$, and HfO$_2$, ZrO$_2$, and so forth, and Ta$_2$O$_5$ may be considered a useful high temperature material at some time in the future.
Despite the good high temperature properties of Ta$_2$O$_5$, tantalum oxidizes very rapidly. Above about 1300°C in air the oxidation reaction proceeds so rapidly that it becomes autogenous. Under these conditions liquid Ta$_2$O$_5$ forms on the surface of the tantalum. At lower oxygen pressures or at lower temperatures the oxidation process proceeds in a normal manner, usually following a linear rate law. Ta$_2$O$_5$ does not form a protective layer on tantalum, and this is partially due to cracking and splitting of the oxide. The oxide to metal volume ratio is high for tantalum, and coupled with new oxide formation occurring at the metal-oxide interface, the high volume ratio leads to bilateral stresses that cause the cracking and splitting. Knowledge of the transport processes occurring in the oxide are of great importance in attempting to understand and alter the oxidation process. A determination of the defect structure reveals which is the mobile specie and the thermodynamics of its formation. For Ta$_2$O$_5$ oxygen ions are expected to be mobile; however, the manner in which they diffuse and the energetics of the process are of interest.

Previous studies of β-Ta$_2$O$_5$ by another investigator revealed a peculiar p-n transition on changing oxygen pressures. Curiosity about whether this phenomenon would also occur in α-Ta$_2$O$_5$ was one reason for conducting this investigation. The principal reason, however, was the hope that by
revealing the defect structure of $\alpha$-$\text{Ta}_2\text{O}_5$ the usefulness of two high temperature materials, tantalum and $\text{Ta}_2\text{O}_5$, might be enhanced.

In this investigation the electrical resistance of an $\alpha$-$\text{Ta}_2\text{O}_5$ sample was measured over a range of oxygen partial pressures at four different temperatures. The data obtained were sufficient to determine the defect structure. A similar attempt to reveal the defect structure of $\text{WO}_2$ at high temperatures was not successful because of the very high intrinsic conductivity of this oxide. The results of the $\text{WO}_2$ investigation and some room temperature conductivity measurements on $\text{MoO}_2$ and $\text{WO}_3$ are given in the Appendix.

Literature Survey

**Tantalum oxides**

The number of oxides formed in the tantalum-oxygen system has been in controversy for some time. There is a preponderance of evidence indicating that $\text{Ta}_2\text{O}_5$ is the only stable oxide in the condensed phases at high temperatures. This opinion is supported by the work of Lagergren and Magneli who heated mixtures of tantalum and $\text{Ta}_2\text{O}_5$ powders at 1100° to 1250°C for prolonged periods and found no evidence of intermediate oxides. Brewer had the same results after heating similar mixtures to 1627°C. Hoch and Mathur could not form intermediate oxides by reacting
tantalum and Ta$_2$O$_5$ mixtures between 1450° and 1815°C. Tourne$^{82}$ was unable to produce intermediate oxides when reducing Ta$_2$O$_5$ with either CaH$_2$ or Al$_2$Ca at temperatures up to 1075°C although he did obtain tantalum in the range from 1050° to 1075°C. Vaughan et al.$^{83}$ determined the solubility of oxygen in tantalum and found Ta$_2$O$_5$ to be the next higher phase in oxygen content. In each of the investigations mentioned X-ray diffraction analysis was used to identify the phases present; and, although in most cases the investigators had hoped to synthesize intermediate oxides, particularly TaO and TaO$_2$, no evidence of oxides other than Ta$_2$O$_5$ was found.

The gaseous molecules, TaO and TaO$_2$, have been studied by several investigators and their works are summarized by Ackerman and Thorn.$^{84}$ Schäfer$^{85}$ investigated the deposits formed by condensing gaseous TaO and TaO$_2$ and found only one oxide present, Ta$_2$O$_5$.

Kofstad$^{86, 87, 88}$ has made an extensive study of the oxidation of tantalum in the temperature range from 500° to 1300°C. His work reveals the formation of three different suboxides, TaO$_y$, TaO$_z$, and TaO. TaO$_y$ and TaO$_z$ form at lower temperatures while TaO forms between 800° and 1200°C. All three oxides are intermediate products of the oxidation reactions, and Kofstad$^{89}$ suggests that these oxides are not thermodynamically stable at high temperatures. Solid oxides
other than $\text{Ta}_2\text{O}_5$ have been reported by Schönberg,\textsuperscript{90} Brauer, Müller, and Kuhner,\textsuperscript{91} Gebhardt and Seghezzi,\textsuperscript{92} and Müller.\textsuperscript{93} Various methods using oxidation of tantalum or reduction of $\text{Ta}_2\text{O}_5$ were used to form these oxides, and in no case were the reported oxides obtained in the pure state. Some of the oxides are the same as those reported by Kofstad,\textsuperscript{86, 87, 88} and the existence of the others as stable phases is questionable.

The stability of $\text{TaO}$ in a very narrow range of oxygen potentials must be considered a possibility. This oxide was found by Kofstad\textsuperscript{88} in oxidation studies, and Lapitskii, Simanov, and Artamonova\textsuperscript{94} obtained $\text{TaO}$ by reducing $\text{Ta}_2\text{O}_5$ with $\text{H}_2$, $\text{Mg}$, $\text{C}$, or $\text{CO}$.

**Tantalum pentoxide**

The existences of two different modifications of $\text{Ta}_2\text{O}_5$ have been confirmed in the work of Lagergren and Magneli,\textsuperscript{79} Reisman et al.,\textsuperscript{95} and Brewer.\textsuperscript{80} The low temperature form is called $\beta$-$\text{Ta}_2\text{O}_5$, and the high temperature form is called $\alpha$-$\text{Ta}_2\text{O}_5$. The transition temperature was reported to be $1520^\circ\pm 20^\circ$C by Lagergren and Magneli\textsuperscript{79} while Reisman et al.\textsuperscript{95} reports $1360^\circ\pm 5^\circ$C. The transformation was found to be sluggish but reversible in both investigations. The melting points of $\text{Ta}_2\text{O}_5$ are $1785^\circ\pm 30^\circ$C for $\beta$-$\text{Ta}_2\text{O}_5$ and $1872^\circ\pm 10^\circ$C for $\alpha$-$\text{Ta}_2\text{O}_5$ according to Reisman et al.\textsuperscript{95} and $1873^\circ\pm 100^\circ$C for $\alpha$-$\text{Ta}_2\text{O}_5$ according to Brewer.\textsuperscript{80}
The temperature for the $\beta$- to $\alpha$-$\text{Ta}_2\text{O}_5$ transformation may be a function of the oxygen pressure. $\alpha$-$\text{Ta}_2\text{O}_5$ was found by Kofstad\textsuperscript{88} at temperatures as low as 1250°C on specimens oxidized in reduced oxygen pressures and by Adelsberg\textsuperscript{96} at temperatures below 1300°C on specimens oxidized in hydrogen-water vapor mixtures.

X-ray diffraction patterns of both modifications of $\text{Ta}_2\text{O}_5$ are complex, and the splitting of lines found by Reisman et al.\textsuperscript{95} prompted him to suggest that the crystal structures are either monoclinic or triclinic. However, Zaslavskii et al.\textsuperscript{97} reports the only complete crystal structure determinations for the oxides, finding $\beta$-$\text{Ta}_2\text{O}_5$ to be orthorhombic and $\alpha$-$\text{Ta}_2\text{O}_5$ to be tetragonal. The results of Zaslavskii et al.\textsuperscript{97} are given in Table 16.

### Table 16

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal Symmetry</th>
<th>Unit Cell Dimensions</th>
<th>Space Group</th>
<th>Cell Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-$\text{Ta}_2\text{O}_5$</td>
<td>orthorhombic</td>
<td>$a_0 = 6.180$ kX</td>
<td>$P2_12_12$</td>
<td>12 $\text{Ta}_2\text{O}_5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b_0 = 43.93$ kX</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c_0 = 3.890$ kX</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$-$\text{Ta}_2\text{O}_5$</td>
<td>tetragonal</td>
<td>$a_0 = 3.80$ kX</td>
<td>$I4/\text{amd}$</td>
<td>6 $\text{Ta}_2\text{O}_5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c_0 = 35.60$ kX</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Two other crystal structure investigations of $\alpha$-Ta$_2$O$_5$ have been reported. Lagergren and Magneli$^9$ indexed powder patterns on an orthorhombic basis, but this work was criticized by Pavlovic$^9$ who demonstrated that the powder data did not allow splitting to be discerned. Pavlovic$^9$ examined single crystals of $\alpha$-Ta$_2$O$_5$ by both optical and X-ray techniques, and he concluded that $\alpha$-Ta$_2$O$_5$ is either monoclinic or triclinic, although twinning effects have caused doubt to be cast on the validity of his data.

The thermodynamics of the tantalum-oxygen have been established by calorimetric methods. Humphrey$^9$ determined the heat of formation of Ta$_2$O$_5$. The heat content of Ta$_2$O$_5$ was determined at low temperature by Kelley$^{10}$ and at high temperature by Orr.$^{11}$ Tables of heats and free energies of formation of Ta$_2$O$_5$ at 100°K intervals from 298.15°K to 3000°K are given by Elliott and Gleiser.$^{12}$ A comparison of the free energy of formation of Ta$_2$O$_5$ with the free energies of formation for other oxides shows that Ta$_2$O$_5$ is relatively stable with about the same stability as Cr$_2$O$_3$ or MnO.

No accurate data were found concerning the homogeneity range of either modification of Ta$_2$O$_5$. Kubaschewski and Hopkins$^{13}$ estimated the range to be TaO$_2$35-25, and they report that Ta$_2$O$_5$ is an n-type conductor. Hartmann$^{14}$ found that the resistance of Ta$_2$O$_5$ increased with increasing oxygen content and concluded that conductivity in Ta$_2$O$_5$ is a reduction phenomenon.
The defect structure of $\beta$-$\text{Ta}_2\text{O}_5$ was studied by Kofstad.\textsuperscript{105} The electrical resistance of a specimen made by sintering pressed oxide powder was measured as a function of oxygen pressure and temperature. Oxygen pressures were fixed with either pure oxygen or CO-CO\textsubscript{2} mixtures. The temperature range covered was from 877° to 1380°C. From the exponential oxygen pressure dependence of the resistance Kofstad\textsuperscript{105} concluded that interstitial oxygen ions were present at high oxygen pressures and oxygen vacancies were present at low oxygen pressures. Maxima in the resistance versus oxygen pressure data were observed which separate the regions of oxygen interstitials and vacancies. The defect structure model was supported by thermoelectric power measurements which change sign from negative to positive on increasing the oxygen pressure at pressures approximately equal to those corresponding to the maxima in the resistance versus oxygen pressure data. Kofstad\textsuperscript{105} suggests that the maxima correspond to approximately stoichiometric $\text{Ta}_2\text{O}_5$ with some anti-Frenkel defect structure present. The activation energy for the resistance at the maxima was assumed to be equal to the value for intrinsic conductivity, and it was used to derive the intrinsic energy gap in $\text{Ta}_2\text{O}_5$, obtaining a value of 3.58eV. The activation energy for the resistance at $10^{-12}$ atm oxygen pressure was determined to
be 50 Kcal/mole, and this value was used to derive a heat of formation of oxygen vacancies of $\geq 150$ Kcal/mole.

Kofstad$^{105}$ also attempted to determine the defect structure of $\beta$-Ta$_2$O$_5$ using a thermogravimetric technique. Very small weight changes were observed in going from one atmosphere O$_2$ to pure CO, and no dependence on oxygen pressure could be derived. Kofstad$^{105}$ concluded that this behavior reflected a very small range of homogeneity and a large heat and free energy of formation of defects.

**Experimental Procedure**

**Specimen preparation**

The Ta$_2$O$_5$ used in this investigation was obtained from the Fansteel Metallurgical Corporation. A chemical analysis of the Ta$_2$O$_5$ lists the following impurities in percentage: Nb$_2$O$_5$--0.01, FeO--0.01, SiO$_2$--0.01, TiO$_2$--0.005, WO$_3$--0.005, ZrO$_2$--0.005, and total alkali--0.001. The Ta$_2$O$_5$ as received was in the form of minus 325 mesh powder. A cylindrical pill of Ta$_2$O$_5$ was made by mixing the Ta$_2$O$_5$ powder with a small amount of glycerine binder and compressing in a steel die at 20,000 psi. The pill was heated to 200°C and held for several hours to remove the glycerine and then heated to 1500°C in a platinum container and held for 40 hours. The 1500°C heat treatment was performed in air in a Burrell furnace having Globar heating.
elements. Seventy per cent theoretical density was achieved by using this heat treatment. X-ray diffraction analysis revealed that only $\alpha$-Ta$_2$O$_5$ was present. An apparent grain size of about 0.5mm was noted on the fracture surfaces of broken specimens prepared by the same technique.

The sintered pill was ground to the shape of a rectangular prism 1mm by 4mm by 12mm using silicon carbide paper and a brass fixture for holding the specimen. The ends of the specimen were coated with platinum by using liquid bright platinum supplied by the Englehard Corporation. The platinum solution was painted on the sample with a small brush, and the sample was then fired at 700°C for 10 minutes. Several layers of platinum were applied. Platinum leads were attached by wrapping 20 mil platinum wire around the specimen at each end.

**Apparatus**

The experimental apparatus consisted of a gas train for supplying gas mixtures of fixed oxygen partial pressure, a Globar furnace, a chamber for equilibrating the specimen with the gas mixture, a Wheatstone bridge with platinum leads to the specimen, and a protected platinum-10% rhodium thermocouple. A schematic diagram of the apparatus is shown in Figure 9.

The gases used to fix the oxygen partial pressures were oxygen, oxygen diluted with argon, carbon dioxide,
Figure 9. Schematic diagram of the apparatus used in the $\alpha$-$\text{Ta}_2\text{O}_5$ defect structure determination.
carbon dioxide diluted with argon, and carbon dioxide–
carbon monoxide mixtures. The argon was passed over hot
Ti chips to remove impurities such as water vapor, oxygen,
and so forth. \( \text{CO}_2, \text{CO}, \) and \( \text{O}_2 \) were passed through magnesiu
perchlorate to remove traces of water vapor, and
the CO was also passed through ascarite to remove traces
of \( \text{CO}_2 \). Each gas passed through a flow meter that had
been calibrated by using a soap film displacement method.

When oxygen was used, the oxygen partial pressure
was calculated from the flow rates of oxygen and argon.
When \( \text{CO}_2 \) or \( \text{CO}_2-\text{CO} \) mixtures were used, the oxygen partial
pressures were calculated from the flow rates of the gases
and the equilibrium constants for the reaction

\[
2\text{CO} + \text{O}_2 = 2\text{CO}_2
\]

at the indicated temperatures. The equilibrium constants
were calculated from the standard free energy equation

\[
\Delta F^\circ = -135000 + 41.5T
\]

for the reaction as given by Kubaschewski and Evans.\(^\text{106}\)
Corrections were made for deviation of the atmospheric
pressure from 760mm Hg when \( \text{CO}_2 \)-argon or \( \text{O}_2 \)-argon mixtures
were used.

The furnace was built according to Globar Corpora-
tion drawing No. EX-1029. The temperature was controlled
by a Wheelco Capacitrol Controller with a saturable
reactor. The furnace chamber was a Morganite Triangle RR alumina tube 38mm ID x 48mm OD x 800mm long with one end closed. The gas mixtures were preheated in an alumina tube which passed down through the chamber.

The specimen was supported only by the platinum leads from the Leeds and Northrup Wheatstone bridge. These leads were placed in an alumina insulator which was attached to the alumina thermocouple protection tube by platinum wire. A 20 mil platinum-10% rhodium thermocouple was used. It had been calibrated at the melting points of gold and silver by the wire method. The thermocouple emf was measured with a Rubicon potentiometer with external batteries, standard cell, and galvanometer.

Test procedure

After the apparatus was assembled the furnace was heated to 1404°C as rapidly as possible to avoid any chance of forming $\beta$-Ta$_2$O$_5$ while heating. The specimen was held at 1404°C in pure oxygen until the resistance became constant. The oxygen was then diluted with argon, and the resistance measured in progressive steps until oxygen partial pressures of about 0.01 atmosphere were reached. The oxygen was then replaced with carbon dioxide, and the same process was repeated. After constant resistance in CO$_2$ partial pressures of about 0.1 atmosphere was reached, carbon monoxide was added and the CO$_2$/CO ratio varied over the
range from 100 to 0.2. The process was then repeated at
another temperature.

Results and Discussion

Experimental data

The resistance of the $\alpha$-Ta$_2$O$_5$ specimen was deter-
mined at four different temperatures from 1404° to 1499°C
in oxygen pressures ranging from 1 to $10^{-9}$ atmospheres. The data are summarized in Table 17 and presented graph-
ically in Figure 10.

The time required to reach constant resistance
values after a change of the atmosphere or temperature
was always very short. Equilibration periods of one hour
or more were allowed for changes of the atmosphere. During
these periods the resistance would remain virtually con-
stant except for the initial change that occurred in a few
minutes after changing the flow rates of the gases. Sev-
eral times the experimental conditions were held constant
for 12 hours or more, and no significant changes in the
resistance were observed during these periods. The very
short response times of $\alpha$-Ta$_2$O$_5$ are similar to those found
by Kofstad$^{105}$ in $\beta$-Ta$_2$O$_5$.

For a given set of experimental conditions the tem-
perature would vary less than $\frac{10^6}{\pi}$°C. The temperature would
shift slightly with changes in the gas flow rates, and, to
Table 17
Resistance Versus Oxygen Pressure and Temperature for α-Ta₂O₅

<table>
<thead>
<tr>
<th>Temperature (°C) ±Std. Deviation</th>
<th>Atmosphere P₀₂, P₀₂ in atm</th>
<th>-logP₀₂</th>
<th>Resistance (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1403.9 ± 0.4</td>
<td>P₀₂ = 0.9860 0.4220 0.1876 0.0948 0.0203 0.0040</td>
<td>0.006 0.375 0.727 1.023 1.693 2.367</td>
<td>29.9 32.1 34.5 38.1 47.6 61.0</td>
</tr>
<tr>
<td>1403.7 ± 0.6</td>
<td>P₀₂ = 0.9853 0.3590 0.1471</td>
<td>3.050 3.305 3.601</td>
<td>76.3 85.2 93.8</td>
</tr>
<tr>
<td>1404.1 ± 0.3</td>
<td>P₀₂/P₀₂ = 61.8 58.5 45.2 25.4 24.8 14.4 6.15 2.30 0.43</td>
<td>4.952 5.001 5.225 5.723 5.745 6.242 6.958 7.812 9.262</td>
<td>73.1 71.4 64.7 52.5 52.0 42.2 31.0 23.7 14.2</td>
</tr>
<tr>
<td>1454.3 ± 0.4</td>
<td>P₀₂ = 0.9927 0.2854 0.0556 0.0198</td>
<td>0.003 0.545 1.255 1.702</td>
<td>27.3 29.5 33.9 38.9</td>
</tr>
<tr>
<td>1454.9 ± 1.0</td>
<td>P₀₂ = 0.9927 0.2958 0.1180 0.1022</td>
<td>2.874 3.224 3.490 3.532</td>
<td>53.5 62.3 67.6 66.8</td>
</tr>
<tr>
<td>1455.9 ± 0.2</td>
<td>P₀₂/P₀₂ = 98.5 40.2 20.3 13.4 8.54 5.07 2.48 1.09 0.43</td>
<td>4.026 4.804 5.400 5.762 6.150 6.613 7.226 7.934 8.738</td>
<td>50.8 37.5 29.7 25.4 22.1 18.9 15.2 12.1 9.40</td>
</tr>
<tr>
<td>Temperature (°C) ±Std.Deviation</td>
<td>Atmosphere $\text{PO}_2, \text{PCO}_2$ in atm</td>
<td>$-\log\text{PO}_2$</td>
<td>Resistance (ohms)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------</td>
<td>-----------------</td>
<td>------------------</td>
</tr>
<tr>
<td>$1482.1 \pm 0.5$</td>
<td>$\text{PO}_2 = 0.9930, 0.2740, 0.02675, 0.01068, 0.0362, 0.0109$</td>
<td>$0.003, 0.562, 0.573, 0.971, 1.441, 1.963$</td>
<td>$25.8, 27.6, 29.1, 31.0, 33.2, 37.6$</td>
</tr>
<tr>
<td>$1482.8 \pm 0.8$</td>
<td>$\text{PCO}_2 = 0.9940, 0.6795, 0.0719$</td>
<td>$2.783, 3.149, 3.544$</td>
<td>$46.4, 51.0, 52.8$</td>
</tr>
<tr>
<td>$1497.6 \pm 1.0$</td>
<td>$\text{PO}_2 = 0.9930, 0.3370, 0.0728, 0.0145$</td>
<td>$0.003, 0.472, 1.138, 1.838$</td>
<td>$28.6, 30.5, 34.0, 38.2$</td>
</tr>
<tr>
<td>$1498.0 \pm 0.8$</td>
<td>$\text{PCO}_2 = 0.9930, 0.3435, 0.2235$</td>
<td>$2.736, 3.043, 3.168$</td>
<td>$44.6, 47.2, 48.3$</td>
</tr>
<tr>
<td>$1499.4 \pm 0.8$</td>
<td>$\text{PCO}_2, \text{PCO}_2$</td>
<td>$3.987, 4.818, 5.388, 5.489$</td>
<td>$33.5, 23.4, 18.7, 18.2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.255, 6.749, 7.747, 8.242$</td>
<td>$14.0, 11.6, 8.64, 7.25$</td>
</tr>
</tbody>
</table>
Figure 10. Log-log plot of resistance versus $P_{O_2}$ for $\alpha$-Ta$_2$O$_5$. 
some extent, it seemed to be dependent on the bases present. Therefore, the temperatures were averaged and standard deviations of the temperature were calculated for each type of atmosphere. These data are given in Table 17.

The flow rates of the gases varied less than 1% during the periods when the resistance was measured. Average values of the flow rates were used in computing the partial pressures and ratios shown in Table 17, and no attempt was made to calculate the standard deviations for these quantities. The small variations in flow rates are not expected to contribute a significant error, especially considering that important quantity for analysis of the data is the $\log P_0^2$.

Once the resistance reached a stable level for a given set of conditions it varied less than $\pm 0.1$ ohm, usually in a random manner. Resistance measurements were made with current passing in alternate directions, and the difference was always less than 0.1 ohm. Average values of the resistance for a given set of conditions are given in Table 17. Since the logarithm of the resistance is the quantity to be analyzed, the minor variations of the resistance are not considered to be significant sources of error.
Isothermal oxygen pressure dependence of the resistance

The logarithmic plot of the resistance versus oxygen pressure given in Figure 10 shows a family of four curves. With the exception of the high oxygen pressure data at 1499°C, the curves are quite similar in shape. Maxima in the region $\log P_{O_2} = -3$ to $-4$ separate regions of completely different dependence on the oxygen pressure. The data in either of the regions can be fitted to an equation of the type

$$ R = A P_{O_2}^n, \quad (73) $$

or

$$ \log R = B + n \log P_{O_2}. \quad (74) $$

For oxygen pressures less than those at the maxima the sign of $n$ in equations (73) and (74) is positive while at higher pressures than the maxima $n$ is negative.

The data for oxygen pressures below the maxima were treated to a least squares analysis based on equation (74). The results are given in Table 18. A similar treatment of the data at high oxygen pressures was not attempted because a close examination of a plot of these data shows changes in slope for each curve and there are not enough data in each of these sub-regions to justify the least squares analysis.

The values for the slopes of the curves at high oxygen pressures were obtained by visual inspection for
Table 18

Least Squares Analysis of the Data at Low Oxygen Pressures Using $\log R = B + n\log P_0$

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$B$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1404.1</td>
<td>2.6742</td>
<td>0.1662</td>
</tr>
<tr>
<td>1455.9</td>
<td>2.3153</td>
<td>0.1557</td>
</tr>
<tr>
<td>1483.8</td>
<td>2.2362</td>
<td>0.1587</td>
</tr>
<tr>
<td>1499.4</td>
<td>2.1092</td>
<td>0.1529</td>
</tr>
</tbody>
</table>

pressures near the maxima and for pressures near one atmosphere. These values are given in Table 19.

Table 19

Slope of $\log R$ versus $\log P_0$ Curves for High Oxygen Pressures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$n$ (near maximum)</th>
<th>$n$ (near $P_0=1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1403.8</td>
<td>-0.151</td>
<td>-0.086</td>
</tr>
<tr>
<td>1454.6</td>
<td>-0.132</td>
<td>-0.081</td>
</tr>
<tr>
<td>1482.4</td>
<td>-0.110</td>
<td>-0.076</td>
</tr>
<tr>
<td>1497.8</td>
<td>-0.075</td>
<td>-0.065</td>
</tr>
</tbody>
</table>

Isobaric temperature dependence of the resistance

The isobars of the resistance versus temperature are expected to follow a relationship of the form
where \( E \), the activation energy, is a constant. Values of \( E \) were calculated for several isobars and these are given in Table 20.

Table 20
Activation Energies for Resistance of \( \alpha\text{-Ta}_2\text{O}_5 \) for Various Isobars

<table>
<thead>
<tr>
<th>( \log P_{O_2} )</th>
<th>( E ), cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10,500</td>
</tr>
<tr>
<td>-1</td>
<td>16,000</td>
</tr>
<tr>
<td>-2</td>
<td>25,200</td>
</tr>
<tr>
<td>-3</td>
<td>33,000</td>
</tr>
<tr>
<td>-5</td>
<td>68,400</td>
</tr>
<tr>
<td>-6</td>
<td>68,000</td>
</tr>
<tr>
<td>-7</td>
<td>66,300</td>
</tr>
<tr>
<td>-8</td>
<td>64,700</td>
</tr>
</tbody>
</table>

The \( E \) values for oxygen pressures down to \( 10^{-3} \) atm were calculated using the slope of a plot of \( \log R \) versus \( T^{-1} \). This plot is shown in Figure 11. The \( \log R \) values for 1499°C were not used in these calculations since they obviously do not line up with the other data. The \( \log R \) values used in the calculations of \( E \) for oxygen pressures from \( 10^{-5} \) to \( 10^{-8} \) were calculated from the least squares
Figure 11. $\log R$ versus $10^4/T$ for $\alpha$-Ta$_2$O$_5$ at high oxygen pressures.
equations given in Table 18. A least squares analysis was then used to calculate the $E$ values in this range. A plot of the calculated $\log R$ values versus $10^4/T$ is shown in Figure 12.

**Defect structure models for Ta$_2$O$_5$**

Four types of defect may be present in Ta$_2$O$_5$, namely oxygen vacancies, oxygen interstitials, tantalum vacancies, and tantalum interstitials; and each may be partially or completely ionized. Electrical conduction may arise from the presence of one or more types of ionized defects and from intrinsic ionization. Relationships between the concentrations of the defects, the oxygen pressure, and the resistance of the oxide may be derived by investigating the various equilibria involving defects, electrons, and so forth.

The methods of formulating the reactions involving defects and the atomic notation for defects in the following analysis are based on the treatment of defects by Kroger and Vink. A defect structure involving oxygen vacancies may be described by using the following chemical reactions:

\[
\frac{1}{2} O_2^{-2} = \frac{1}{2} O_2(g) + V_o ,
\]

(a)

\[
V_o = V_o^* + \theta ,
\]

(b)

and

\[
V_o^* = V_o^{**} + \theta .
\]

(c)
Figure 12. logR versus $10^4/T$ for $\alpha$-$\text{Ta}_2\text{O}_5$ at low oxygen pressures.
\( O_{1}^{2-} \) represents an oxygen ion on a normal lattice site, \( V_{o} \) is an oxygen vacancy with two trapped electrons, \( V_{o}^{+} \) is a singly ionized oxygen vacancy, \( V_{o}^{2-} \) is a doubly ionized oxygen vacancy, and \( \Theta \) denotes a free or conduction electron. The oxygen vacancies are assumed to form donor levels in the band structure which may contribute free electrons on ionization. These donor levels are expected to be near the conduction band. Equilibrium constants for the reactions may be derived by applying the law of mass action as follows:

for reaction (a) \( K_{a} = [V_{o}]P_{O_{2}}^{1/2} \),

for reaction (b) \( K_{b} = \frac{[V_{o}^{+}]\Theta}{[V_{o}]} \),

and for reaction (c) \( K_{c} = \frac{[V_{o}^{2-}]\Theta}{[V_{o}^{+}]} \).

The bracketed symbols in equations (76), (77), and (78) denote concentrations. A concentration term for \( O_{1}^{2-} \) is not included in equation (76) since this quantity is very large and virtually constant. The use of concentrations of the defects and electrons instead of activities in equations (76), (77), and (78) is justified where these concentrations are very small, and this is expected to be the case for \( Ta_{2}O_{5} \).

An additional source of conduction electrons is intrinsic ionization, which may be described by the reaction...
ground state = $\Theta + \Theta$. \hspace{1cm} (d)

$\Theta$ denotes a free electron hole in the valence band. The equilibrium constant for the intrinsic ionization reaction is

$$K_d = [\Theta] [\Theta].$$ \hspace{1cm} (79)

A condition of electro-neutrality for the oxide must be imposed as follows:

$$[\Theta] = [V_o^+] + 2[V_o^{2-}] + [\Theta].$$ \hspace{1cm} (80)

This equation states that the total number of conduction electrons is the sum of those ionized from the oxygen vacancies (which act as donors) and those thermally excited to the conduction band according to reaction (d). Three limiting conditions may be considered:

I. for $[\Theta] \gg [V_o^+] + 2[V_o^{2-}]$, $[\Theta] = [\Theta]$,

II. for $[V_o^+] \gg 2[V_o^{2-}] + [\Theta]$, $[\Theta] = [V_o^+]$,

and

III. for $2[V_o^{2-}] \gg [V_o^+] + [\Theta]$, $[\Theta] = 2[V_o^{2-}]$.

Combining the expressions for $[\Theta]$ for each condition with the appropriate equilibrium constant equations leads to the following:

for I., $[\Theta] = \frac{K_d^{1/2}}{P_{O_2}^{1/4}}$. \hspace{1cm} (81)

for II., $[\Theta] = (K_a K_b)\frac{1/2}{P_{O_2}^{1/4}}$. \hspace{1cm} (82)

and

for III., $[\Theta] = (2K_a K_b K_c)\frac{1/2}{P_{O_2}^{1/4}}$. \hspace{1cm} (83)
For the first condition the concentration of electrons is independent of the oxygen pressure, and for the second and third conditions the concentration of electrons is given by a constant times the oxygen pressure raised to some negative, fractional exponent. Of course, the equilibrium constants are exponential functions of the temperature.

Other defects could contribute either electrons or electron holes to the conduction processes, and a chemical reaction may be written for each case as follows:

for oxygen interstitials, \[ \frac{1}{2} \text{O}_2(g) = O_{i}^{n-} + n\Theta, \]

for tantalum interstitials, \[ \frac{1}{2} \text{Ta}_2\text{O}_5 = \text{Ta}_{i}^{n+} + n\Theta + \frac{5}{4} \text{O}_2(g), \]

and for tantalum vacancies, \[ \frac{5}{4} \text{O}_2(g) = \frac{5}{2} O_{1}^{-2} + v_{Ta}^{-n} + n\Theta. \]

In these equations the subscript \( i \) denotes an interstitial ion and \( n \) is an integer denoting the state of ionization of the defect. For oxygen interstitials, \( n \) has a maximum value of 2, and for either tantalum defect the maximum value of \( n \) is 5. In formulating the reaction involving oxygen interstitials and tantalum vacancies, these defects are assumed to form acceptor levels so that electron hole formation will result on ionization of the defect. Similarly, the tantalum interstitials are assumed to form donor levels contributing free electrons on ionization. The relative positions of these donor and
acceptor levels in the band structure of $\alpha$-Ta$_2$O$_5$ are not known, but some speculation about the position of the oxygen interstitial level will be given later. Another complete set of reactions may be postulated in which the valence of the defect changes sign and the opposite type of carrier is involved. For example, the tantalum interstitial may act as an electron trap taking on a negative valence and, thus, creating a free electron hole. Reactions of this type are possible but very unlikely to occur because of the high ionization energies involved. These reactions will not be considered further.

Using the condition of electro-neutrality and limiting conditions where only one kind of defect is present, the exponent of the oxygen pressure in the equation for either electron or electron hole concentration was derived for each kind of defect. These exponents and the source and identity of the conducting specie are given in Table 21. In Table 21 the exponents of the oxygen pressure are negative for oxygen vacancies and tantalum interstitials and positive for oxygen interstitials and tantalum vacancies. The positive and negative exponents are associated with electron holes and electrons, respectively.
Table 21
Exponents for Oxygen Pressure Dependence of Electron or Electron Hole Concentration

<table>
<thead>
<tr>
<th>Source and Identity of Conducting Specie</th>
<th>Exponent of Oxygen Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Conduction, θ and Φ</td>
<td>0</td>
</tr>
<tr>
<td>V⁺₀</td>
<td>-0.250</td>
</tr>
<tr>
<td>V⁻₀</td>
<td>-0.167</td>
</tr>
<tr>
<td>Ta⁺</td>
<td>-0.625</td>
</tr>
<tr>
<td>Ta⁺²</td>
<td>-0.416</td>
</tr>
<tr>
<td>Ta⁺³</td>
<td>-0.313</td>
</tr>
<tr>
<td>Ta⁺⁴</td>
<td>-0.250</td>
</tr>
<tr>
<td>Ta⁺⁵</td>
<td>-0.208</td>
</tr>
<tr>
<td>O⁻ᵢ⁻¹</td>
<td>+0.250</td>
</tr>
<tr>
<td>O⁻ᵢ⁻²</td>
<td>+0.167</td>
</tr>
<tr>
<td>V⁻Ta⁻¹</td>
<td>+0.625</td>
</tr>
<tr>
<td>V⁻²Ta⁻¹</td>
<td>+0.416</td>
</tr>
<tr>
<td>V⁻³Ta⁻¹</td>
<td>+0.313</td>
</tr>
<tr>
<td>V⁻⁴Ta⁻¹</td>
<td>+0.250</td>
</tr>
<tr>
<td>V⁻⁵Ta⁻¹</td>
<td>+0.208</td>
</tr>
</tbody>
</table>
Deduction of the defect structure of $\alpha$-Ta$_2$O$_5$

The resistance of a material is related to the resistivity, $\rho$, by the equation

$$ R = \frac{\rho}{\ell A} $$

(84)

where $\ell$ and $A$ are the length and area, respectively. If only one kind of carrier participates in the conduction process, the resistivity is given by

$$ \rho = \frac{(NC\mu)^{-1}}{} $$

(85)

where $N$ is the concentration of charge carriers, $C$ is the charge per carrier, and $\mu$ is the carrier mobility. The fundamental quantity related to the defect structure is $N$, although both $N$ and $\mu$ are related to the resistance by

$$ R \propto (N\mu)^{-1} $$

(86)

and both $N$ and $\mu$ may be functions of the oxygen pressure and the temperature. To deduce the defect structure of an oxide, one must examine both the isothermal oxygen pressure dependence of $R$ and the isobaric temperature dependence of $R$ and attempt to separate out the effects of $N$ and $\mu$.

Since two distinct types of behavior of the resistance of $\alpha$-Ta$_2$O$_5$ were observed, each is treated separately. The behavior at low oxygen pressures is treated first because the interpretation is relatively simple and straightforward.

The identity of the defects in $\alpha$-Ta$_2$O$_5$ at low oxygen pressures is deduced by comparing the exponential
oxygen pressure dependence of $R$ given in Table 18 with the theoretical values for the carrier concentration dependence listed in Table 21. Of course, the signs in one set must be reversed due to the inverse relationship between $R$ and $N$. A very favorable comparison is realized for the doubly ionized oxygen vacancy model. The theoretical value of $n$ of 0.167 is nearly equal to the experimental values which range from 0.153 to 0.166.

A further test of the defect structure model is shown in Figure 13 where the resistance is plotted versus $P_n^{1/6}$. For all four isotherms the resistance data are linear functions of $P_n^{1/6}$. This supports the doubly ionized oxygen vacancy model. The slightly positive $R$ intercepts shown in Figure 13 are probably due to the small lead resistance (less than one ohm) which was ignored in the analysis of the data. The near zero intercepts demonstrate that the principal contribution to conduction is from the proposed defects and that intrinsic ionization does not occur. From the latter observation, one may conclude that the energy gap in $\alpha$-$\text{Ta}_2\text{O}_5$ is relatively large.

The activation energies for the resistance of $\alpha$-$\text{Ta}_2\text{O}_5$ at low oxygen pressures are listed in Table 20. Interpretation of these activation energies is complicated by a lack of knowledge about the band structure of $\text{Ta}_2\text{O}_5$ and the temperature dependence of the mobility. Morin$^{108}$
Figure 13. Resistance versus $P_{O_2}^{1/6}$ for $\alpha$-$Ta_2O_5$ at low oxygen pressures.
suggested that Ta$_2$O$_5$ has a narrow, normally empty d band, and the work of Janninck and Whitmore indicates that a similar oxide, Nb$_2$O$_5$, has a narrow d band with conduction caused by oxygen vacancies acting as donors. The temperature dependence of the mobility for conduction in a narrow d band would be quite different from that for a "hopping" type mechanism. The mobility for the latter mechanism is an exponential function of temperature and often dominates the activation energy for conduction. For d band conduction, the temperature dependence on the mobility is not expected to be dominant, and it is often ignored. Since Ta$_2$O$_5$ is expected to display d band conduction and the temperature interval of this investigation is very short, it is assumed that the mobility is virtually independent of temperature. Based on this assumption the association of the heat of formation of the defects with the activation energy may be demonstrated.

The temperature dependencies of the equilibrium constants for reactions (a), (b), and (c) in the previous section are given by

\[ K_a = K_a^0 e^{-\Delta H_v/RT}, \]  \hspace{1cm} (87)

and

\[ K_b = K_b^0 e^{-E_1/RT}, \]  \hspace{1cm} (88)

\[ K_c = K_c^0 e^{-E_2/RT}. \]  \hspace{1cm} (89)
The pre-exponential terms, $K_0^a$, $K_0^b$, and $K_0^c$ are assumed to be temperature independent. $\Delta H_v$ denotes the heat of formation of oxygen vacancies having two trapped electrons, and $E_1$ and $E_2$ denote the ionization energies for the first and second trapped electrons, respectively. Combining equations (87), (88), and (89) into equation (83) leads to

$$\Theta = \left(2K_0^aK_0^bK_0^c\right)^{1/2}P_0/2 \exp\left(-\frac{\Delta H_v + E_1 + E_2}{2RT}\right).$$

Thus, the activation energy for the resistance at low oxygen pressures is assumed to be approximately equal to the quantity $(\Delta H_v + E_1 + E_2)/3$. An average value for the activation energy at low oxygen pressures is 67,000 cal/mole, and it is concluded that $(\Delta H_v + E_1 + E_2)$ is equal to 201,000 cal/mole.

The values of $E_1$ and $E_2$ are expected to be quite small according to Kroger and Vink who use approximations based on the ionization of a hydrogen atom and a helium ion in a dielectric medium. The value of $E_1$ is estimated by substituting an approximate value of the dielectric constant, $\varepsilon$, into the equation

$$E_1 \approx \frac{310500}{\varepsilon^2}, \text{cal/mole}.$$  

Pavlovic found $\varepsilon$ values for $\alpha$-$\text{Ta}_2\text{O}_5$ ranging from 30 to 10,000 at temperatures from 77 to 377°K. If a minimum value of 30 for $\varepsilon$ is assumed, a value of about 350 cal/mole for $E_1$ results. The value of $E_2$ is estimated from
to be 1400 cal/mole. An approximate value of $\Delta H_v$ of 200,000 cal/mole is obtained on substitution of the estimated values of $E_1$ and $E_2$.

The value of $(\Delta H_v + E_1 + E_2)$ found in this investigation may be compared to values for $\beta$-Ta$_2$O$_5$ and $\alpha$-Nb$_2$O$_5$ since these oxides have similar defect structures. Kofstad\textsuperscript{105} determined a value of 150,000 cal/mole for $\beta$-Ta$_2$O$_5$. The value 103,000 cal/mole for $\alpha$-Nb$_2$O$_5$ was also determined by Kofstad.\textsuperscript{111} The relatively large value of $\Delta H_v$ should lead to a very narrow range of homogeneity for $\alpha$-Ta$_2$O$_5$. This view is not unreasonable, and it is supported by observations of this author that weight losses by samples of $\alpha$-Ta$_2$O$_5$ melted in a vacuum could not be detected although the color always changed from white to black.

It is concluded that at low oxygen pressures the resistance of $\alpha$-Ta$_2$O$_5$ is dominated by the presence of doubly ionized oxygen vacancies contributing electrons to a d type conduction band, and that the activation energy for the resistance principally reflects the heat of formation of the oxygen vacancies. Accordingly, $\alpha$-Ta$_2$O$_5$ has an oxygen deficient structure at low oxygen pressures, and the diffusion of oxygen should be considerably faster than that of tantalum.

\[ E_2 > 4E_1 \]
Interpretation of the experimental data obtained at high oxygen pressures is difficult. The isothermal oxygen pressure dependence of the resistance is complex, and the activation energies for the resistance are strongly oxygen pressure dependent. The data obtained at 1499°C are particularly difficult to include in the analysis. The defect structure may be deduced but with less confidence about its accuracy.

Values of the exponent, n, for the oxygen pressure dependence of the resistance are shown in Table 19, and by changing signs in one set these may be compared to the theoretical values in Table 21. The values obtained at 1404° and 1455°C at oxygen pressures near the maxima are -0.151 and -0.132, respectively, and these are reasonably close to the theoretical value for a doubly ionized oxygen interstitial. The other values of n are much smaller than any predicted values but are significantly greater than zero to discount intrinsic ionization.

The linearity of the resistance with $P_{O_2}^{1/6}$ was graphically checked for each temperature. A reasonably good correlation was obtained in some instances, but the data were not sufficient to provide a valid test. Kofstad, who encountered difficulty in interpreting his resistance data near one atmosphere oxygen pressure, noted that marker studies of the oxidation of tantalum have demonstrated that oxygen is mobile in Ta$_2$O$_5$ at one atmosphere and that
this favored the oxygen interstitial defect over the tantalum vacancy in $\beta$-$\text{Ta}_2\text{O}_5$. Similar behavior might be expected for $\alpha$-$\text{Ta}_2\text{O}_5$.

The small values of $n$ and the changes in $n$ at high oxygen pressures may be due to one or more effects. An interaction of defects would invalidate the law of mass action approach which is based on the assumption that the concentrations are so small that each defect acts independently of the others. Activity coefficients which may be functions of the composition would have to be incorporated into the theoretical carrier concentration equations, and this could lead to complex oxygen pressure dependence. It is possible that interactions would occur at relatively small concentrations when the large oxygen ion is placed in an interstitial site.

The characteristics of the acceptor levels formed in band structure by the oxygen interstitials are not known, but in seeking an explanation of the behavior at high oxygen pressures one may speculate regarding their characteristics. If the acceptor levels are formed above the valence band and the levels split on increasing concentration of oxygen interstitials, conduction behavior similar to that observed in this investigation could result. For the conditions where $n$ is near $-0.167$, the concentrations are less than those where splitting of the acceptor levels occurs, and
conduction is principally dependent on the defect concentration. As the temperature or oxygen pressure is increased the concentration of defects increases and splitting occurs with some levels moving away from and some moving nearer to the valence band. Thus, although the total number of oxygen interstitials would increase, the number near enough to the valence band to be ionized would be restricted, and the resistance would tend toward a limiting value. This model could also account for the anomalous behavior at 1499°C. However, this acceptor level splitting explanation is purely speculative; and, in the absence of information on the band structure of Ta$_2$O$_5$, it should be regarded with skepticism. A complex band structure that is a function of both oxygen pressure and temperature is a possibility for α-Ta$_2$O$_5$.

The activation energies for the resistance at high oxygen pressures are listed in Table 20, and a variation from 33,000 cal/mole at 10$^{-3}$ atmospheres to 10,500 cal/mole at one atmosphere oxygen pressure may be noted. The shift of the activation energy with oxygen pressure is related to the changes in the n values. One must conclude that more than one process is involved in determining the electrical properties of α-Ta$_2$O$_5$ at high oxygen pressures, particularly if the data at 1499°C are assumed to be valid. A defect structure involving oxygen interstitials which
form a range of acceptor levels could account for the temperature dependence of resistance since this model requires both the energy to form the defects and an oxygen pressure dependent ionization energy.

A very rough approximation of the heat of formation of oxygen interstitials in $\alpha$-$\text{Ta}_2\text{O}_5$ may be made by using the activation energy of the resistance at $10^{-3}$ atmospheres oxygen pressure. It is assumed that for this value of oxygen pressure the resistance behavior is dominated by the presence of doubly ionized oxygen interstitials which contribute two electron holes per defect to the valence band. Neglecting the temperature dependence of mobility, the activation energy is equal to $(\Delta H_1 + E_1' + E_2') / 3$ where $\Delta H_1$ is the heat of formation of oxygen interstitials and $E_1'$ and $E_2'$ are the ionization energies for the addition of the first and second electrons, respectively. There is no simple way to estimate values for $E_1'$ and $E_2'$, and for this case it is best to assume $E_1'$ and $E_2'$ are zero. Thus a very rough value of $\Delta H_1$ equal to 99,000 cal/mole is derived.

No contribution to conduction from intrinsic ionization was found in this investigation. For the low oxygen pressures, it was demonstrated that intrinsic ionization did not occur; and, at high oxygen pressures, intrinsic ionization would have caused quite different behavior. It is concluded that the energy gap in $\alpha$-$\text{Ta}_2\text{O}_5$ is quite large, probably several eV.
The maxima in the resistance at intermediate oxygen pressures separate n or electron type conductivity at low oxygen pressures from p or electron hole type conductivity at high oxygen pressures. The maxima probably correspond to stoichiometric $\alpha$-$\text{Ta}_2\text{O}_5$. The sharp changes in the oxygen pressure dependence at the maxima indicate that only very small concentrations of both defects are present. An anti-Frenkel structure in $\alpha$-$\text{Ta}_2\text{O}_5$ comparable to that proposed by Kofstad$^{105}$ for $\beta$-$\text{Ta}_2\text{O}_5$ may be present over a very narrow range of oxygen pressures. The maxima shift to lower oxygen pressures with increasing temperature principally because of the difference in the heats of formation of the defects. Similar maxima and changes from p to n type conductivity have been observed in $\beta$-$\text{Ta}_2\text{O}_5$ by Kofstad,$^{105}$ in Cu$_2$O by Toth et al.$^{112}$ and in Fe doped TiO$_2$ by Rudolph.$^{113}$

It is concluded from this investigation that $\alpha$-$\text{Ta}_2\text{O}_5$ has a complex defect structure at high temperatures with an anion deficiency at low oxygen pressures and an anion excess at high oxygen pressures. The anion deficient structure results from the presence of doubly ionized oxygen vacancies, and the heat of formation of oxygen vacancies is about 200,000 cal/mole. The anion excess structure is due to the presence of oxygen interstitials, and a very rough approximation of the heat of formation of oxygen interstitials is 99,000 cal/mole.
Hopefully, more work on $\alpha$-$\mathrm{Ta}_2\mathrm{O}_5$ will be carried out in the future. Properly executed electrical resistance and thermoelectric power measurements on single crystal specimens should lead to a more satisfactory picture of the conduction mechanisms. Information about the band structure and energy gap in $\alpha$-$\mathrm{Ta}_2\mathrm{O}_5$ would be helpful in interpreting the conduction behavior.
CONCLUSIONS

The following conclusions were deduced from the experimental observations of the three investigations reported in this work:

1. The standard free energy of formation of ReO₂(c) is given by the equation

\[ \Delta F_{\text{ReO}_2}^0 = -102750 + 40.67T(\text{cal/mole}) \]

for temperatures from 950° to 1100°K.

2. ReO₃ does not melt but decomposes according to the reaction

\[ 3\text{ReO}_3(c) = \text{ReO}_2(c) + \text{Re}_2\text{O}_7(g) \]

with the partial pressure of Re₂O₇(g) reaching one atmosphere at approximately 913°K.

3. The standard free energy of formation of Mo₄O₁₁(c) is given by the equation

\[ \Delta F_{\text{Mo}_4\text{O}_{11}}^0 = -679500 + 223.3T(\text{cal/mole}) \]

for temperatures from 920° to 1090°K.

4. Mo₄O₁₁ decomposes according to the peritectic reaction
\[ \text{Mo}_4\text{O}_{11}(c) = \text{MoO}_2(c) + 3\text{MoO}_3(l) \]

at 1098°C.

5. \( \alpha\text{-Ta}_2\text{O}_5 \) has a complex defect structure in the temperature range from 1404°C to 1499°C for oxygen partial pressures from one to \( 10^{-9} \) atmospheres. Maxima in the electrical resistance were observed at intermediate oxygen partial pressures separating regions where different defects dominate the conduction processes. At high oxygen pressures, \( \alpha\text{-Ta}_2\text{O}_5 \) is an anion-excess, p-type semiconductor with doubly ionized oxygen interstitials present. A very rough approximation of the heat of formation of the oxygen interstitial is 99,000 cal/mole. At low oxygen pressures \( \alpha\text{-Ta}_2\text{O}_5 \) is an anion-deficient, n-type semiconductor with doubly ionized oxygen vacancies present, and the heat of formation of the oxygen vacancy is approximately 200,000 cal/mole. The resistance data at high oxygen pressures were not simple functions of the oxygen pressure or temperature, and this may reflect a complex band structure for \( \alpha\text{-Ta}_2\text{O}_5 \). The energy gap for \( \alpha\text{-Ta}_2\text{O}_5 \) is expected to be large because intrinsic conduction did not occur at temperatures up to 1500°C.
Some Observations of the Electrical Conductivities of WO$_2$, WO$_3$, and MoO$_2$

High temperature measurements of the electrical conductivity of polycrystalline WO$_2$ were made in an effort to determine the defect structure of this oxide. The conductivity displayed metallic characteristics and was independent of the oxygen partial pressure; and, thus, contributions to the conductivity by defects were overshadowed. Room temperature measurements were made on single and polycrystalline samples of MoO$_2$ and on single crystals of WO$_3$ to determine the magnitudes of their electrical conductivities. The conductivities of all three oxides are of interest in relation to their band structures.

Tungsten powder of 99.99+% purity supplied by Amend Drug and Chemical Company was oxidized in CO-CO$_2$ gas mixtures to WO$_2$. Compacts of the WO$_2$ were made in a steel die and sintered at 1400°C in an argon atmosphere for 60 hours. By using the same method, the polycrystalline samples of MoO$_2$ were made from 99.9% purity molybdenum powder supplied by Fansteel Metallurgical Corporation. The single crystals of MoO$_2$ were made by reacting MoO$_2$ and MoO$_3$ in a sealed
vycor capsule at 850°C for several days followed by slowly cooling to room temperature. Crystals up to 1 mm on edge and approximately cubic in shape were obtained. The single crystals of WO$_2$ were grown by vapor deposition during a study of the reactions between tungsten oxides and H$_2$-H$_2$O gas mixtures. The starting material was 99.98% WO$_2$ supplied by A. D. Mackay, Incorporated. The single crystals were needle shaped with typical dimensions approximately 0.1 mm by 0.5 mm by 10 mm. The identities of the WO$_2$ and MoO$_2$ were checked by X-ray powder techniques. The single crystal character of the MoO$_2$ was determined by back reflection methods. The WO$_2$ crystals were determined to be in the tetragonal or high temperature modification with one "a" axis parallel to the needle axis by using a precession camera. Some evidence of twinning in the WO$_2$ crystals was noted.

The electrical conductivity of WO$_2$ was measured by using a four probe technique with both direct and alternating current. CO-CO$_2$ gas mixtures were used to stabilize the WO$_2$. The temperature was measured with a calibrated platinum-10% rhodium thermocouple. The conductivity measurements at room temperature were made with a Kelvin bridge. Average values of the conductivities are listed in Table 22.

The conductivities of all three oxides are relatively high, approaching the range for metallic substances.
Table 22

Electrical Conductivities of WO₂, WO₃, and MoO₂

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature</th>
<th>Conductivity (ohm⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polycrystalline WO₂</td>
<td>710°C</td>
<td>2.4(10)³</td>
</tr>
<tr>
<td></td>
<td>805°C</td>
<td>1.8(10)³</td>
</tr>
<tr>
<td></td>
<td>980°C</td>
<td>1.5(10)³</td>
</tr>
<tr>
<td>(65% theoretical density)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>single crystal WO₃</td>
<td>25°C</td>
<td>8(10)²</td>
</tr>
<tr>
<td>single crystal MoO₂</td>
<td>25°C</td>
<td>1.1(10)³</td>
</tr>
<tr>
<td>polycrystalline MoO₂</td>
<td>25°C</td>
<td>6(10)²</td>
</tr>
<tr>
<td>(68% theoretical density)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The temperature coefficient of the conductivity of WO₂ is negative which is a characteristic of metallic materials.

Magneli and Marinder¹⁵ have demonstrated that there are short metal-metal distances in WO₂ and MoO₂, and Morin¹⁰⁸ shows that d orbital overlap in transition metal compounds may lead to metallic range conductivities. There are two excess d electrons for each metal atom in either WO₂ or MoO₂, and high conductivities would result if a d band were present. The existences of d bands in WO₂ and MoO₂ are supported by this investigation.

The conductivity values for tetragonal WO₃ may be compared to values of approximately 10 to 30 ohm⁻¹ cm⁻¹ found by Lawley¹¹⁴ for polycrystalline WO₃ at high temperatures for oxygen pressures near one atmosphere. The much
higher value found in this investigation is probably caused by a considerable departure from stoichiometry since the single crystals were deposited in an atmosphere with an oxygen partial pressure several orders of magnitude less than one. Lawley\textsuperscript{114} proposes that the defects in tetragonal WO$_3$ are oxygen vacancies; and, if a high concentration of oxygen vacancies was quenched into the single crystals, it is possible that these defects would act as donors at room temperature, contributing electrons to a normally empty d band. This would confirm the suggestion of Morin\textsuperscript{108} that the d orbital overlap in WO$_3$ is sufficient to give metallic properties on departure from purity or stoichiometry.

In summary, the high conductivities of WO$_2$, WO$_3$, and MoO$_2$ are believed to reflect partially filled d bands which act as conduction bands. For WO$_2$ and MoO$_2$ the d band is partially filled intrinsically, and for WO$_3$ the partial filling results from a deviation from stoichiometry.
BIBLIOGRAPHY


39. Ibid., p. 214.


72. Kubaschewski and Evans, p. 258.


77. Kubaschewski and Evans, p. 187.


89. P. Kofstad, Central Institute for Industrial Research, Blindern, Oslo, Norway, private communication.


96. L. M. Adelsberg, The Ohio State University, Columbus, Ohio, private communication.


98. A. S. Pavlovic, "An Optical and Crystallographic Study of the High Temperature Form of Ta_2O_5," West Virginia University, Morgantown, West Virginia, private communication, unpublished research.


102. Elliott and Gleiser, p. 203.


